

Conductivity Behavior of Sodium and Potassium Aluminosilicate Glass Melts

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The electrical conductivity was investigated in two series of alkali aluminosilicate glass melts, $25R_2O(R: Na \text{ and } K)-xAl_2O_3-(75-x)SiO_2$ at temperatures ranging from 1000 to 1400°C. The dependences of conductivity or activation energy on Al_2O_3/R_2O of both series in the molten state showed a same behavior. These results in the molten state were compared with previous studies for sodium alkali aluminosilicate glasses in the molten and solid state, and explained in terms of the binding state: $[-O]^-R^+$ and $[AlO_4]^-R^+$.

Key words : Electrical conductivity, Alkali aluminosilicate glass melts, Al_2O_3/R_2O , Molten state, Solid state, Binding state

I. Introduction

It is well known that alkali aluminosilicate ($R_2O-Al_2O_3-SiO_2$) glasses show a higher electrical conduction in the range of $Al_2O_3/R_2O < 1$ when SiO_2 is replaced by Al_2O_3 .^{1,2)} But if the mole ratio, Al_2O_3/R_2O is larger than 1, the conduction begins to decrease. Therefore, the electrical conductivity shows a maximum at $Al_2O_3/R_2O=1$ with Al_2O_3 replacement. This behavior is known as the aluminium oxide anomaly. It is generally agreed that this anomaly derives from a coordination change of Al surrounded with oxygen (from tetrahedral to octahedral).³⁻⁵⁾

The most experimental works related to the above electrical conduction of alkali aluminosilicate glasses were performed below transformation temperature ($< T_g$). From the viewpoint of the glass structure, it is important to compare the conductivity behaviors between below and above T_g . Because of the devitrification of glasses and the difficulties to measure the conductivity at high temperature, especially in the molten state, only one study⁶⁾ on sodium aluminosilicate glass melts has been carried out in the range of $Al_2O_3/Na_2O < 1$. Its results, however, exhibited opposite behavior in the solid state (below T_g) and the molten state (above T_g) as SiO_2 is progressively replaced by Al_2O_3 (Fig. 1). In several works^{7,8)} the conductivity behaviors of sodium aluminosilicate glasses below T_g have been discussed by using the model of Anderson and Stuart⁹⁾ in which the activation energy (E_a) for ionic conduction consists of electrostatic bond energy (E_b) required to remove an ion from its charge compensating center (for example, $[-O]^-Na^+$ or $[AlO_4]^-Na^+$) and strain energy (E_s) that the ion need to expend in passing through a doorway in network. Accordingly, it can be postulated that the pure influence of Al_2O_3 , in other words the effect of electrostatic bond en-

ergy between Na^+ and $[AlO_4]^-$ on conductivity can be observed only above T_g where the strain energy may be free.

The main objective of this work is to examine whether such a conductivity behavior above T_g for sodium aluminosilicate glasses is available for another alkali ions. Therefore, in the present work the conductivity was measured not only in sodium-(SAS) but also potassium aluminosilicate (PAS) glass melts. The observed results are discussed here relative to the role of Al_2O_3 in the glass structure.

II. Experimental Procedure

1. Glass preparation

Glass melts of mol % composition $25Na_2O-xAl_2O_3-(75-x)SiO_2$ and $25K_2O-xAl_2O_3-(75-x)SiO_2$ with $x=0, 5, 7.5, 10$, in which the Al_2O_3/R_2O (n) mole fraction ($R_2O: Na_2O \text{ \& } K_2O$) took the values 0, 0.2, 0.3 and 0.4, were examined. All of the glasses studied lie beyond the composition range for the metastable phase separation.¹⁰⁾ The starting materials, high purity quartz sand, commercial reagent grade Na_2CO_3 , K_2CO_3 and $Al(OH)_3$ were mixed thoroughly and melted in an electrically heated furnace at temperatures ranging from 1450 to 1700°C, depending on the given composition. All glasses were melted in Pt/5Au crucibles. Sufficient time (4-10 hours) was allowed for the melts to become visibly homogeneous and bubble-free. The glass melts were then cast into a graphite mould to give conductivity cell-crucible shaped specimens and annealed near their transformation temperature. These glasses were remelted in the conductivity cell for the measurement.

Wet chemical analysis of the glasses was carried out to examine the possible compositional changes during melt-

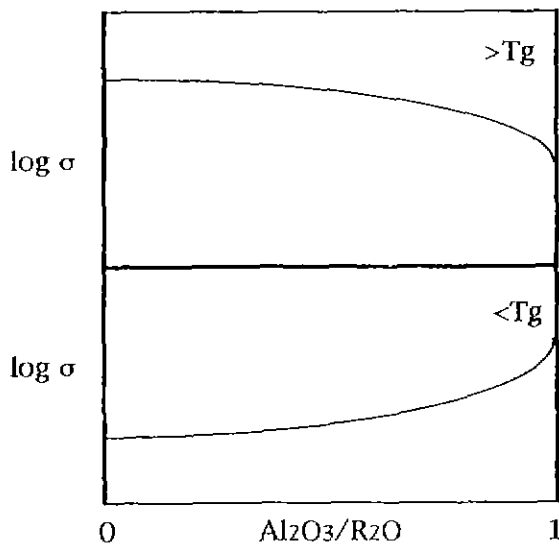


Fig. 1. Schematic diagram for electrical conductivity versus $\text{Al}_2\text{O}_3/\text{R}_2\text{O}$ of alkali aluminosilicate glasses in the molten state ($>T_g$) and the solid state ($<T_g$).

ing. The results indicated a deviation from batch composition of less than 1 mol % of alkali oxide.

2. Melt conductivity measurement

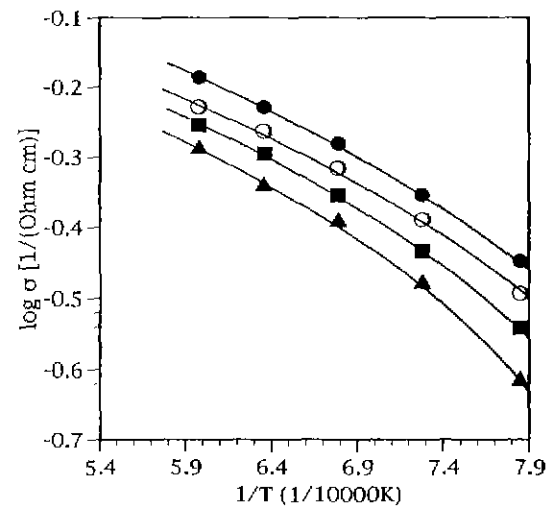
For the electrical measurement of glass melts, a conductivity cell with two electrodes was applied. The cell is constituted by an alumina crucible filled with glass melt and by the two Pt/30Rh electrodes placed on below melt level. Electrical conductivity is measured between two electrodes separated by a distance 18 mm. As a measurement bridge, an impedance bridge in the range 40 Hz to 4 KHz (Digital-Konduktometer Type 600, Knick, Germany) was used. The conductivity measurements were performed at 4 KHz where the polarisation of electrode can be ignored.¹¹ The cell was calibrated direct at high temperature between 1000-1300°C with several molten glasses. As glass melts for the calibration, binary alkali silicate glass systems $20\text{Na}_2\text{O}-80\text{SiO}_2$ and $20\text{K}_2\text{O}-80\text{SiO}_2$ were used. The details of the measuring procedure and the cell arrangement are described elsewhere.^{12,10}

The reproducibility of glass melt conductivity was also measured. Conductivities obtained were reproducible within less than 5%. After calibration of the cell, conductivities of glass melts were measured at 100 K temperature intervals within temperature range 1000 to 1400°C.

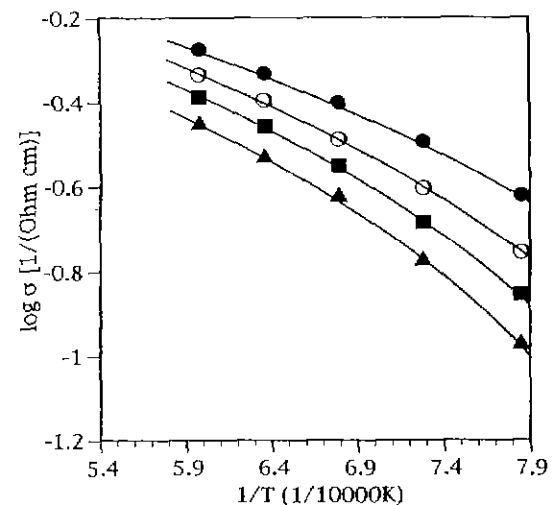
III. Results and Discussion

1. Dependence of temperature

The temperature dependence of conductivity (σ) for sodium-(SAS) and potassium aluminosilicate (PAS) glass melts are presented respectively as the plots of $\log \sigma$ versus the reciprocal absolute temperature ($1/T$) in Fig.



(a) $25\text{Na}_2\text{O}-x\text{Al}_2\text{O}_3-(75-x)\text{SiO}_2$



(b) $25\text{K}_2\text{O}-x\text{Al}_2\text{O}_3-(75-x)\text{SiO}_2$.

Fig. 2. Temperature dependence of electrical conductivity (σ) in alkali aluminosilicate glass melts, $n=\text{Al}_2\text{O}_3/\text{R}_2\text{O}$, ●: $n=0$, ○: $n=0.2$, ■: $n=0.3$, ▲: $n=0.4$.

2(a) and (b). It is known that many inorganic glass-forming liquids exhibit the non-Arrhenius behavior in the wide temperature range above T_g . The non-Arrhenius behavior in conductivity against $1/T$ of all the present glasses can be best expressed by least squares curve fitting as a second-degree polynomial of the type: $\log \sigma = A + B/T + C/T^2$ where A, B and C are constants. By first differentiation of this equation activation energy for the ion conduction can be calculated. As shown in Fig. 2 the conductivity decreases with increasing n ($\text{Al}_2\text{O}_3/\text{R}_2\text{O}$) at constant temperature. This behavior is clearly demonstrated by the activation energy values.

Fig. 3 shows the average activation energy (E_σ) of SAS and PAS glasses in temperature range 1000-1400°C as a function of $\text{Al}_2\text{O}_3/\text{R}_2\text{O}$. Table 1 contains also the activation energy values corresponding to each glass. As ex-

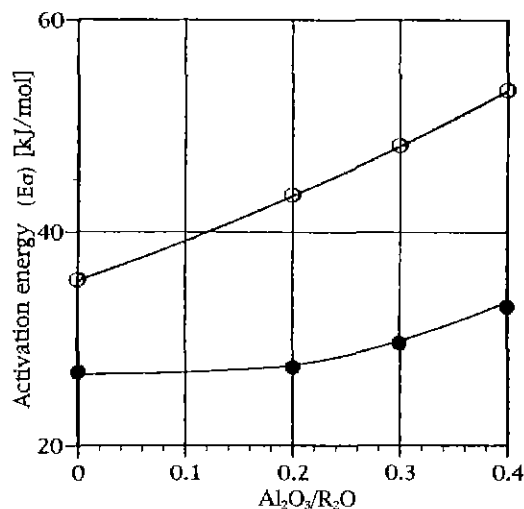


Fig. 3. Average activation energy (E_a) of SAS (●) and PAS (○) glasses in temperature range 1000-1400°C as a function of Al_2O_3/R_2O .

Table 1. Average Activation Energy (E_a) for Ion Conduction in the Temperature Range 1000-1400°C in Sodium-(SAS) and Potassium Aluminosilicate (PAS) Glass Melts

Al_2O_3/R_2O (n)	$E_{a/SAS}^*$ (kJ/mol)	$E_{a/PAS}^{**}$ (kJ/mol)
0	26.8	35.4
0.2	27.3	43.4
0.3	29.5	48.1
0.4	32.9	53.3

*SAS: $25Na_2O-xAl_2O_3-(75-x)SiO_2$.

**PAS: $25K_2O-xAl_2O_3-(75-x)SiO_2$.

pected from the temperature dependence in Fig. 2, the activation energy increases with increasing Al_2O_3/R_2O . PAS glasses have a higher activation energy than that of SAS. It is well known that the mobility of alkali ions depends on not only their field strength but also their radius. In the case of binary sodium-(SS) and potassium silicate (PS) glasses, in spite of its lower field strength the K ion has a larger radius than Na ion and, thus the activation energy for ion mobility or conduction of PS glasses is higher than SS.¹⁰ This is also valid for PAS and SAS glasses. The influence of Al_2O_3 on the conductivity is in detail explained in the next section.

2. Influence of Al_2O_3

Fig. 4 presents conductivity isotherms of both alkali aluminosilicate glass melts, as a function of Al_2O_3/R_2O mole fraction at 1000, 1200 and 1400°C. The conductivity decreases with Al_2O_3 -substitution independent of kind of alkali oxide. In other words, the mobility of alkali ions decreases by introduction of Al_2O_3 . This tendency for conductivity of both glass series shows a good agreement with that of SAS of Wakabayashi.⁹ It can be thus suggested that such a conductivity behavior on Al_2O_3/R_2O is also available for another alkali aluminosilicate glass

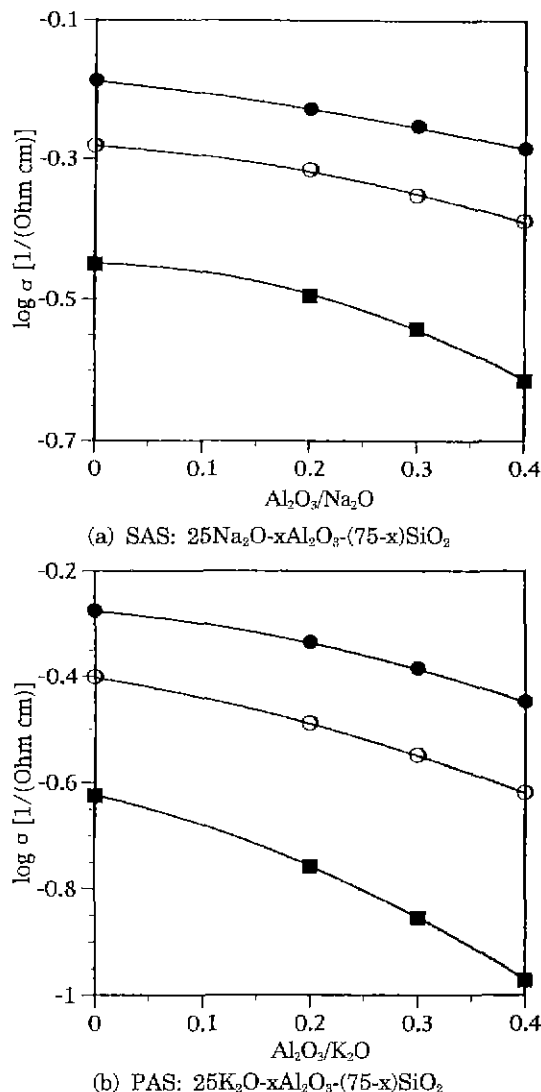


Fig. 4. Compositional dependence of the electrical conductivity (σ) against Al_2O_3/R_2O in alkali aluminosilicate glass melts, ●, 1400°C, ○: 1200°C, ■: 1000°C.

melts.

It is generally agreed that when SiO_2 is substituted by Al_2O_3 in alkali silicate glasses in the range of $Al_2O_3/R_2O < 1$, the aluminium ion goes into tetrahedral coordination as a network former [AlO_4] which eliminates the non-bridging oxygens^{9,10} and, thus strengthens the total glass network, for example glass viscosity.¹⁵ Charge neutrality of [AlO_4] tetrahedra is maintained by the presence of alkali ions, which broke up the network and created non-bridging oxygen [-O]. The alkali ions can then be bound with the two types of sites: [-O]-R⁺ and [AlO_4]-R⁺ where the content of the nonbridging oxygens ([-O]-R⁺) decreases with increasing Al_2O_3 content ([AlO_4]-R⁺). The decrease of the ion mobility or conductivity by Al_2O_3 -substitution in Fig. 4 can be explained with this change of alkali ion binding state, assuming that the binding energy of [AlO_4]-R⁺ is stronger than that of [-O]-R⁺.

Based on the behavior below T_g (lower part of Fig. 1), it was mentioned in several literatures¹⁶⁻¹⁸⁾ that the alkali ion is stronger bonded with the nonbridging oxygen than with $[\text{AlO}_4]^-$ and, hence the alkali ion mobility increases with the replacement of SiO_2 by Al_2O_3 . According to simple calculation using an electrostatic model,^{8,10)} in the solid state (below T_g) the binding energy of the $[\text{AlO}_4]^- \text{R}^-$ appears to be lower than that of $[-\text{O}]-\text{R}^+$ because of larger radius of $[\text{AlO}_4]^-$. But this can not explain the conductivity behavior in the molten state of Fig. 4 (or upper part of Fig. 1). This inconsistency was discussed by the work of Wakabayashi⁷⁾ in which besides the change of alkali ion binding state, the effect of different thermal histories on alkali ion mobility was considered in the solid state, namely the conductivity in solid state does not simply depend on the composition, but on the glass structure in equilibrium with the frozen temperature ($\approx T_g$) from melt to glass. Recent study of Hsieh⁹⁾ indicated that the activation energy (E_a) for ion conduction below T_g is a sum of binding energy (E_b) and strain energy (E_s). In practice the conductivity of glasses below T_g is strongly dependent on their thermal history, for example cooling rate.¹⁹⁾ On the other hand, it can not be postulated that the conductivity in the molten state depends on the thermal history. Therefore, in the molten state where the strain energy due to thermal history is excluded, it seems to be clear that only the binding energy between anion and alkali ion plays a role of activation energy. Based on the structural information and the conductivity behaviors discussed above, it may be suggested that the binding energy of $[\text{AlO}_4]^- \text{R}^-$ is stronger than that of $[-\text{O}]-\text{R}^+$. But in order to confirm this suggestion, it must be performed to determine the binding energies of both types theoretically by using reasonable parameters.

IV. Summary

The electrical conductivities of two series of alkali aluminosilicate glasses, $25\text{Na}_2\text{O}-x\text{Al}_2\text{O}_3-(75-x)\text{SiO}_2$ and $25\text{K}_2\text{O}-x\text{Al}_2\text{O}_3-(75-x)\text{SiO}_2$ were measured in the molten state (1000-1400°C). All the melts of both glass-series showed a same conductivity behavior. Their conductivities decreased with increasing $\text{Al}_2\text{O}_3/\text{R}_2\text{O}$. The activation energy for conduction of both series showed also a same behavior. From the present results it was concluded that such a behavior is also available for another alkali aluminosilicate glass melts.

Additionally, the influence of Al_2O_3 on the conductivity was discussed. On the base of the structural information in alkali aluminosilicate glasses and the opposite behavior of their conductivity in the solid state and the molten state it was suggested that the binding state of $[\text{AlO}_4]^- \text{R}^-$ is stronger than that of $[-\text{O}]-\text{R}^+$.

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