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Contents

Ionic Conductivity of xM_2O . (1-X) B_2O_3 Glass

Soe Soe Thin

Abstract

Addition of alkali ions (Na^+, K^+) to the borate glass system greatly affects its electrical conductivity. Results of a systematic study of the influence of alkali ions M on the conductivity of $M_2O.B_2O_3$ (M= Na, K) glass system are reported. Samples were prepared with the ratio of $xM_2O.(1-x)\ B_2O_3$ where ($0.05 \leq x \leq 0.25$). The dc electrical measurements were made over a temperature range of 423-693K. It is found that the conductivity increases with temperature and with the increase in the M_2O content. The activation energy decreases with increasing M_2O content.

Key Words: Ionic conductivity, Sodium borate glass, Potassium borate glass.

Introduction

In recent years, much attention is focused on superionic conducting glasses because of their ionic conduction and application to the batteries and other electrochemical devices(Dwivedi,B.P.&Khanna,B.N.,1994). Electrical conduction in glasses has acquired great technological importance, particularly after the discovery of fast ion conduction in glassy materials. Different types of glasses have been subjected to detailed study to see whether the conductivity can be manipulated to be suitable for various technological applications(Brow, R.K.,2003, Haines, P. J.,1995).It is well known that glasses containing alkali ions are essentially cationic conductors, the current being carried by relatively mobile alkali ions. The motion of alkali ions in a glass is important not only because of its relation to electrical conductivity, but also to chemical durability and to ion exchange kinetics (Dormus, R. H.,1973, Dwivedi, B. P. & Khanna, B.N.,1994). The study of glass structure is important because the properties exhibited by the glasses are both composition and structure sensitive (Dormus, R. H.,1973).

The glass system x M_2O. (1-x) B_2O_3 ($0.05 \leq x \leq 0.25$) known as alkali oxide glass is characterized by a high resistance. The addition of alkali oxide in this system greatly affects the conductivity (John,V.,1992). The purpose of the present paper is to clarify whether the conduction

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behavior differs between low and high concentration of alkali ion glasses. Alkali ion concentration dependence of ionic conductivity for the glasses is investigated as a function of temperature (Haines, P. J.,1995). The result of a systematic study of the influence of alkali ions on the dc electrical conductivity of borate glasses was observed.

Experimental Procedure

Reagent grade H_3BO_3 and M_2O (M=Na,K) are mixed in crucible, $xM_2O.(1-x)B_2O_3$ proportions for $0.05 \le x \le 0.25$. The synthesis and characterization of the M_2O-B_2O_3 glasses have been described. The mixture of the starting materials H_3BO_3 and M_2CO_3 of guaranteed reagent grade was pulverized thoroughly in an agate mortar and then transferred into porcelain crucible. After being pulverized, is malted about 1000°C for an hour in an electric furnace. The samples are made by pouring the bubbles free melt in between the copper mold kept at room temperature. The samples are transparent. The process was shown in Fig 1.

The sample was sandwiched between two copper plates that serve as two electrodes. To ensure better electrical contact, silver paste was applied evenly on both surfaces of the sample. The sample was placed in a sample holder that was immersed in a heating steel chamber surrounded by asbestos. Sample was inserted between two copper plates and filled with silver paste to get good conduct. Each copper plate brought into contact with copper rod from the chamber.

Thermal conducting mica shield is used between the sample and the chamber to have a good thermal conductivity and to protect from electrical conduction. Experimental set-up for conductivity measurement is shown in Fig2 .The resistances were measured using HIOKI mega-ohm tester. The J-type thermocouple was inserted near the sample to record its temperature. The copper block holder was heated by 120 W heater coil and on time of the heater is controlled by C^{++} program. Temperature of the specimen was kept constant with $\pm 1K$ by the PC based temperature controller. The conductivity has been calculated using the formula $\sigma = \frac{l}{RA}$ where l the thickness of the sample, A the area of cross-section of the electrodes and R is the resistance. The conductivity was measured over a temperature range from 423K-693 K at intervals of 20 K.

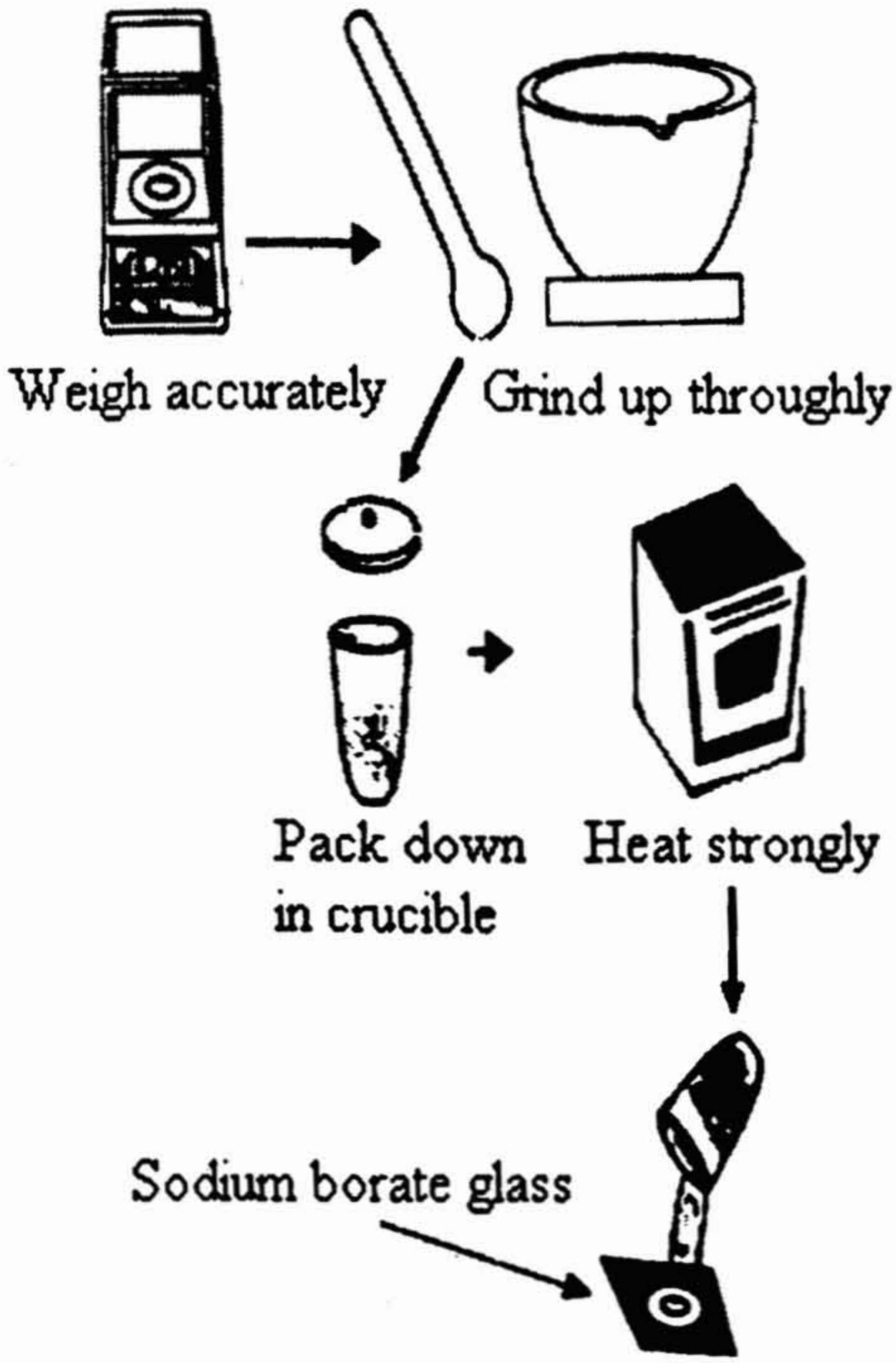

Fig.1. Reaction scheme for the formation of sodium borate glass using the melt-quenching method

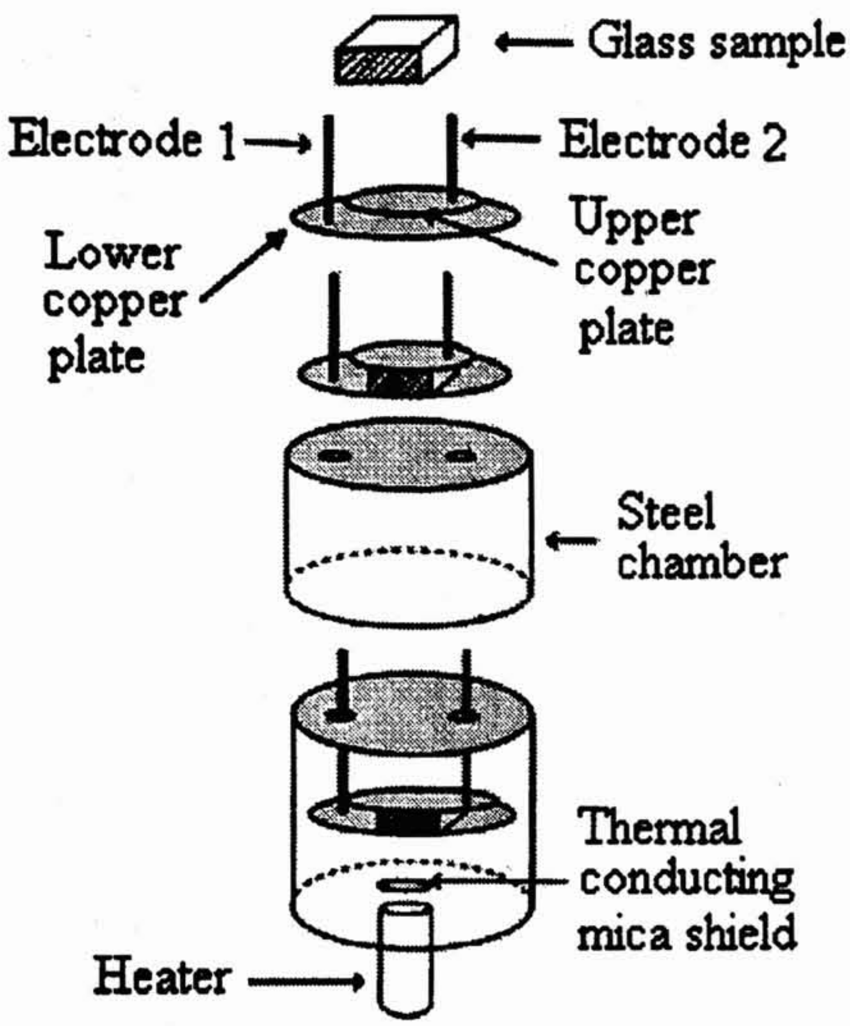

Fig.2. Arrangement for the conductivity measurement

Results and Discussion

Conductivity is a structure sensitive property because the structure decides both the potential barriers for the transport of mobile ions as well as the mobile ion concentration. The structure changes both by increasing temperature and by the concentration of constituents (Anderson, O. L. & Stuart,D.A.,1954).The compositions of the prepared glasses are listed in tables.

Table.1(a). Chemical composition of the prepared glasses

(x Na_2O.(1-x)B_2O_3 glass)

Sample No	(1-x)mol% of B_2O_3	x mol% of Na_2O
1	95	5
2	90	10
3	85	15
4	80	20
5	75	25

Table.1(b).Chemical composition of the prepared glasses

($x\ K_2O\ .(1\text{-}x)B_2O_3$ glass)

Sample No	(1-x)mol% of B_2O_3	x mol% of K_2O
2	85	15
3	75	25
5	50	50

The electrical conductivity of sodium borate and potassium borate glasses have been investigated and in all the temperature dependence of the conductivity followed Arrhenius relation : $\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$ where σ is the conductivity, the σ_0 pre-exponential factor, E_a the activation energy for conduction, k the Boltzmann constant and T the absolute temperature (Dwivedi, B. P. & Khanna, B. N.,1994).

Arrhenious plots of the variation of dc conductivity for the prepared glass sample of sodium borate and potassium borate glasses (shown in Table.1a & b) with temperature (423K- 639K) are shown in Fig.3(a) and 3(b) respectively. From the plot, it is obvious that the conductivity increases with increasing in M_2O concentration and also with temperature expected. Hence, increase in conductivity with increase in M_2Omust be due to the transport of alkali ions. According to the model proposed by Anderson and Stuart, the activation energy must be decreased with an increase of the alkali content resulting in an enhanced conductivity. Table.2 a& b show the variation of activation energy with M_2O content. The results of conductivity in Na_2O-B_2O_3 and K_2O-B_2O_3 glass system strictly agrees with this model (Anderson, O. L. & Stuart, D. A. ,1954). From Table.2 a &b, the results also agree with Anderson and Stuart model.

Table.2(a). Activation energies of the prepared glasses (Na_2O-B_2O_3)

Sample No	$xNa_2O.(1-x)B_2O_3$	Activation energy E_a (eV)
2	$0.10Na_2O.\ 0.90B_2O_3$	2.1104
3	$0.15Na_2O.\ 0.85B_2O_3$	1.0604
4	$0.20Na_2O.\ 0.80B_2O_3$	0.9718
5	$0.25Na_2O.\ 0.75B_2O_3$	0.8434

Table.2(b). Activation energies of the prepared glasses (K_2O-B_2O_3)

Sample No	$xK_2O.(1-x)B_2O_3$	Activation energy E_a (eV)
2	$0.15K_2O.\ 0.85B_2O_3$	1.59
3	$0.25K_2O.\ 0.75B_2O_3$	1.0657
5	$0.50K_2O.\ 0.50B_2O_3$	0.8929

Conclusion

The influence of alkali ions on the dc electrical conductivity of xM_2O-$(1-x)B_2O_3$ glasses has been investigated. It is found that the conductivity increases with temperature as well as with concentration of M_2O.Among the two alkali borate glasses, sodium borate glass is better conductivity than potassium. It is concluded that the enhanced conductivity is due to the effect of alkali ions .The activation energy decreases with increasing M_2O content.

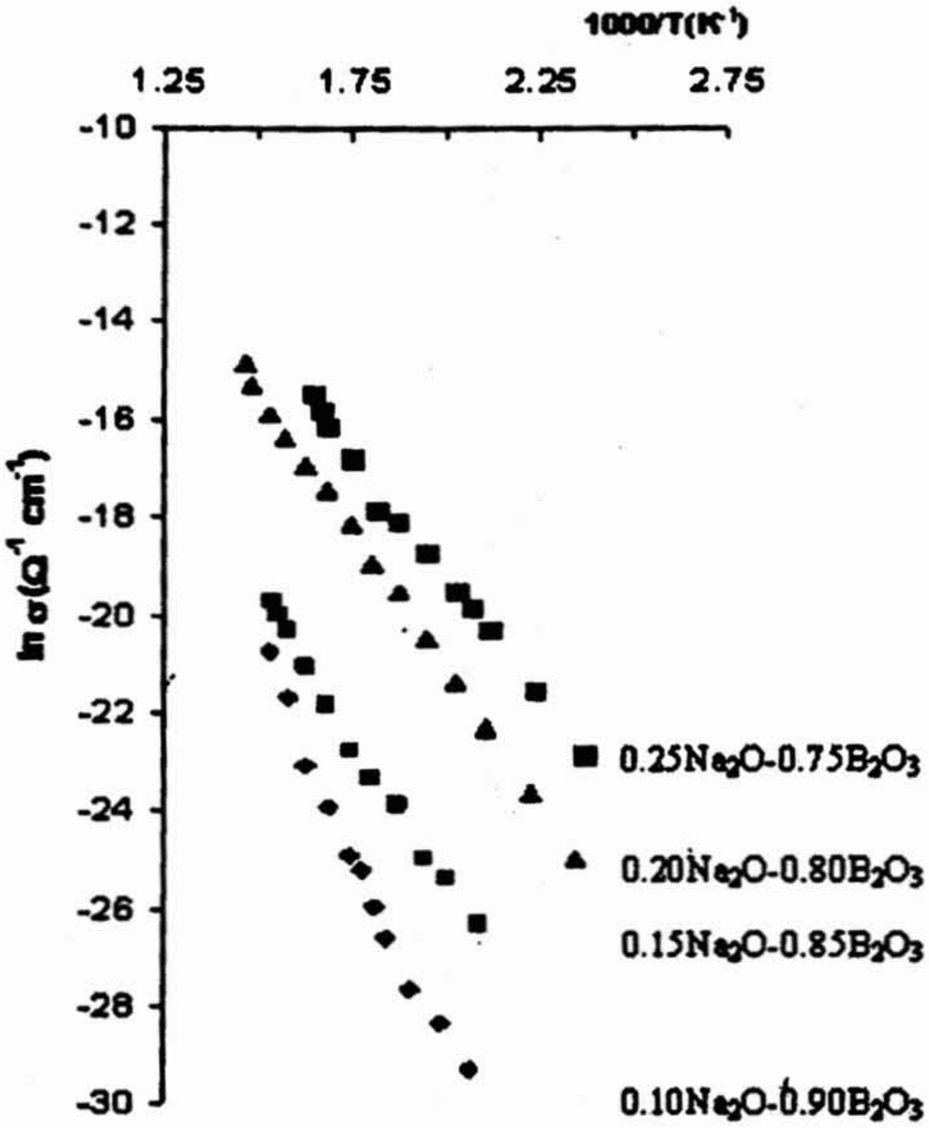

Fig.3(a). Conductivity measurement of xNa_2O-$(1-x)B_2O_3$ glass

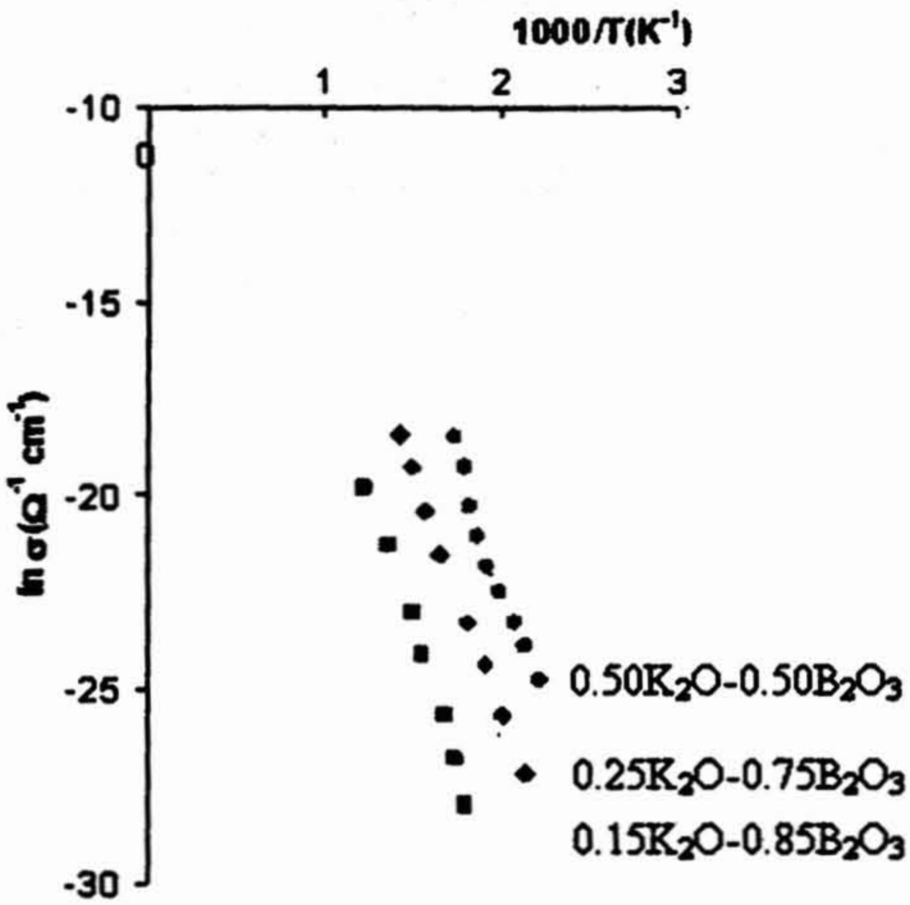

Fig.3(b). Conductivity measurement of xK_2O-$(1-x)B_2O_3$ glass

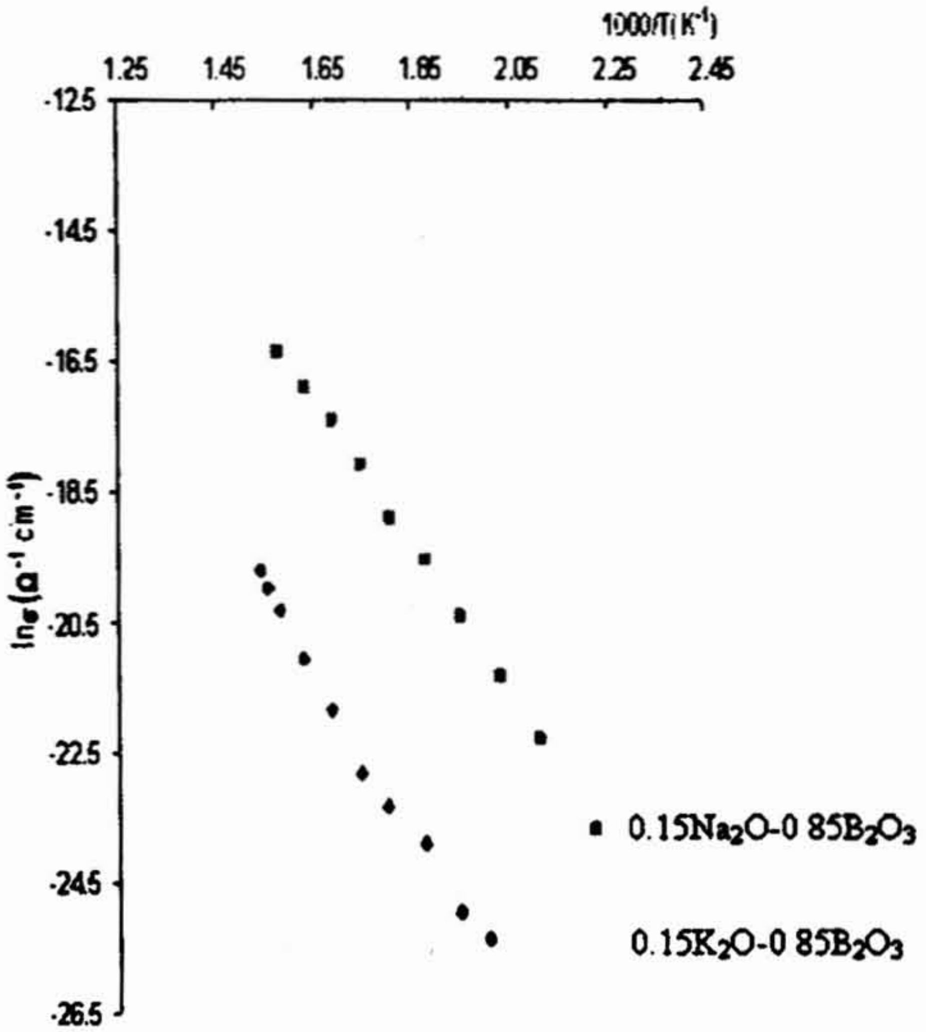

Fig.3(c). Conductivity comparison for xNa_2O-$(1-x)B_2O_3$ glass and xK_2O-$(1-x)B_2O_3$ glass (x =0.15)

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