

Ion transport mechanism in borate glasses: Influence of network structure on non-Arrhenius conductivity

S. Murugavel^{1,2,*} and B. Roling^{2,3}

¹*Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany*

²*Sonderforschungsbereich 458, Westfälische Wilhelms-Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany*

³*Fachbereich Chemie, Physikalische Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, D-35032 Marburg, Germany*

(Received 4 October 2007; published 16 November 2007)

In this paper, we report a non-Arrhenius behavior in the temperature-dependent dc conductivity of alkali ion conducting borate glasses below their glass transition. This behavior is strongly influenced by the alkali oxide content and by the type of the alkali ions, and is most pronounced in glasses with low alkali oxide content and with large alkali ions. In contrast to many fast ion conducting glasses, the curvature in the Arrhenius plot is positive. Furthermore, we show that annealing of the glass samples leads to a partial recovery of the Arrhenius behavior. Our experimental results are interpreted in terms of local structural changes in the borate network with temperature, which have been detected by means of solid state NMR spectroscopy.

DOI: [10.1103/PhysRevB.76.180202](https://doi.org/10.1103/PhysRevB.76.180202)

PACS number(s): 66.30.Hs, 66.10.Ed, 61.43.Fs

Alkali ion diffusion in glasses is an issue of central interest because of its important role in different technological applications, in addition to its fundamental relation to properties such as electrical conductivity, chemical durability, and ion exchange kinetics.¹⁻⁴ An adequate understanding of the temperature and composition dependence of ion transport requires microscopic information on both structure and dynamics. Structural changes occurring during supercooling of a glass-forming liquid contribute an additional source of configurational entropy, which ultimately influences the structural relaxation and transport properties. Therefore the influence of temperature on liquid structure reveals a link between configurational entropy and glass formation and provides important clues to the mechanism of diffusion and viscous flow. Structural defects present in the liquid state may be preserved after quenching and may play an important role for the ion transport in the glassy state.

The ion transport properties of a variety of glass-forming network structures have been studied in numerous investigations; among these systems boron oxide (B_2O_3) is unique in its ability to transform between two local environments. These two local structures are defined by three- and fourfold coordinated boron ($[^3]B$ and $[^4]B$) atoms. A transition from one of these coordinations to the other can be achieved by varying the alkali oxide concentration, temperature or pressure.⁵⁻⁷ Recently, there has been considerable interest in pressure-induced changes in boron coordination.⁷ The manipulation of boron coordination provides considerable opportunity to tailor the physical properties of B_2O_3 containing glasses to match a host of technological needs. The incorporation of alkali oxide to borate is known to cause progressive changes in the boron coordination number from $[^3]B$ to $[^4]B$ as well as the formation of various cyclic units. The relative concentrations of these structural units depend strongly on the concentration and type of the alkali oxide. Statistical thermodynamic modeling as well as shear relaxation studies on borate glasses have suggested the importance of changes in borate speciation with temperature.^{8,9}

These speciation changes can be grouped into two major classes: (i) disintegration of six-membered boroxol rings

(B_3O_6) into nonring BO_3 units, and (ii) dissociation of BO_4 species into symmetric BO_{3S} units (with three B-O-B linkages) and nonbridging oxygen (NBO).^{8,9} As shown by solid-state NMR spectroscopy, the speciation depends also on thermal history, i.e., on the quenching rate.^{6,10,11} Glasses subjected to a higher quenching rate exhibit a higher fictive temperature and contain fewer BO_4 units than do slowly cooled or annealed glass samples. Thus an annealing process leads to a strong modification of the local environment of mobile cations. Such structural modifications are absent in alkali silicate and germanate glasses, where the network structure does not depend strongly on temperature and fictive temperature, respectively.¹² Hence borate glasses are interesting model materials for studying the influence of glass structure on ion transport.

Recently, Mehrer and co-workers carried out electrical conductivity and tracer diffusion measurements on sodium and rubidium borate glasses. From their results they calculated the Haven ratio which is a measure for correlations between movements of different alkali ions.¹³ While the Haven ratio for sodium borate glasses is, within the experimental error, independent of temperature, the Haven ratio of rubidium borate glasses increases with temperature. This suggests a stronger temperature dependence of the network structure of rubidium borate glasses which influences the rubidium ion transport mechanism.

In this paper, we provide information about the influence of the borate network structure on alkali ion transport in more detail by taking frequency- and temperature-dependent conductivity of borate glasses with different compositions and different thermal histories. We find deviations from Arrhenius behavior in their dc conductivity which are influenced by both composition and thermal history, and we show that these deviations can be related to structural peculiarities of the glasses.

Glasses of composition $x Na_2O \cdot (1-x) B_2O_3$ with $0.10 \leq x \leq 0.30$ and of composition $0.20 M_2O \cdot 0.80 B_2O_3$ with $M=Li, Na, K, Rb, \text{ and } Cs$ were prepared by melting dry mixtures of high purity B_2O_3 and the respective alkali carbonate in a platinum crucible under an atmosphere of air.

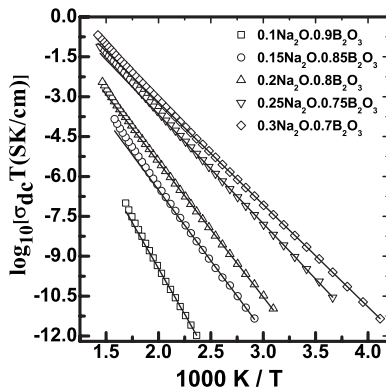


FIG. 1. Arrhenius plot of the dc conductivity (multiplied by the temperature) of $x \text{Na}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$ glasses with $0.10 \leq x \leq 0.30$. The symbols represent experimental data points, while the solid lines are fits to an Arrhenius law.

The melts were held at 1273 K for 3 h in order to get homogeneous liquids and then poured into a stainless steel mold. To diminish internal stresses, as-prepared glass samples were annealed 30 K below their respective glass transition temperatures for 5 h and then cooled to room temperature with a rate of 1 K/min (these samples are referred to as “normal glasses”). Additionally, we have prepared glasses by adopting different quenching and annealing procedures. For this purpose, we used $0.10 \text{Na}_2\text{O} \cdot 0.90 \text{B}_2\text{O}_3$ and $0.30 \text{Na}_2\text{O} \cdot 0.70 \text{B}_2\text{O}_3$ glass samples to test the effect of thermal history on the electrical conductivity. After annealing, the glass samples were ground to their requisite sizes, the surfaces were polished, and metal electrodes consisting of silver and platinum layers were sputtered onto each surface. Conductivity measurements were carried out by using a Novocontrol α -S high-resolution dielectric analyzer in a frequency range from 1 mHz to 3 MHz and in a temperature range from room temperature to about 40 K below the glass transition temperature.

The frequency-dependent conductivity spectra are characterized by well-defined low-frequency plateaux, where the conductivity is identical to the ionic dc conductivity. These plateaux allow the determination of the dc conductivity with an error of less than 2%. In Fig. 1 we present Arrhenius plots of the dc conductivity for normal glasses of composition of $x \text{Na}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$ with $0.10 \leq x \leq 0.30$, measured over a wide range of temperatures. At low temperatures, the measured dc conductivities follow the simple Arrhenius form, i.e.,

$$\sigma_{dc} T = \sigma_0 \exp(-E_a^{dc}/k_B T). \quad (1)$$

In contrast, at higher temperatures, the dc conductivities deviate from the Arrhenius law and exhibit a positive curvature. With increasing alkali oxide content, the onset of non-Arrhenius behavior shifts to higher temperatures and the deviations from Arrhenius behavior become weaker. In order to analyze this behavior in more detail, we have calculated *apparent* activation energies by taking the running slope between adjacent temperature and conductivity points, see Fig. 2. With decreasing alkali oxide content, the temperature de-

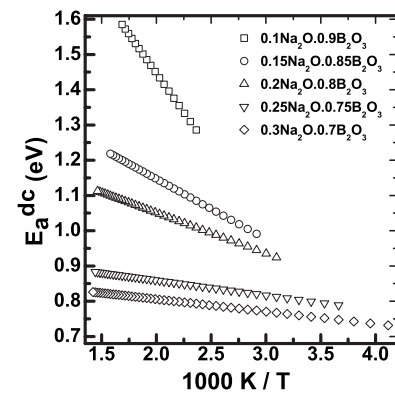


FIG. 2. The variation of the “apparent activation energy” with temperature in $x \text{Na}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$ glasses with $0.10 \leq x \leq 0.30$.

pendence of the apparent activation energy becomes stronger.

These results are complemented by measurements on $0.20 M_2\text{O} \cdot 0.80 \text{B}_2\text{O}_3$ glasses with $M = \text{Li}, \text{Na}, \text{K}, \text{Rb},$ and Cs , where the most pronounced deviation from the Arrhenius behavior is found in cesium borate glass as shown in Fig. 3. We note that these results are in good agreement with earlier investigations by Jain and his co-workers on single alkali and mixed alkali borate glasses.¹⁴ These authors reported that the dc conductivity follows, in a first approximation, an Arrhenius law in the narrow range of temperatures. However, by analyzing the data in more detail with least square fitting analysis, they were able to find non-Arrhenius behavior in both single alkali and mixed alkali borate glasses.

Figure 4 shows the temperature-dependent dc conductivity of a $0.10 \text{Na}_2\text{O} \cdot 0.90 \text{B}_2\text{O}_3$ glass sample with different thermal histories. Both, the as-prepared glass sample (virgin) and the normal glass sample show Arrhenius behavior at low temperatures (narrow range) and deviations from Arrhenius behavior at high temperatures. Here, it is important to note

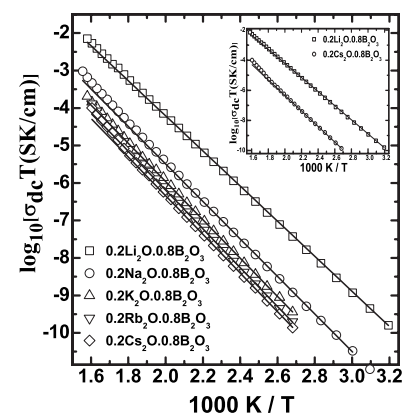


FIG. 3. Arrhenius plot of the dc conductivity (multiplied by the temperature) of $0.2 M_2\text{O} \cdot 0.8 \text{B}_2\text{O}_3$ glasses with $M = \text{Li}, \text{Na}, \text{K}, \text{Rb},$ and Cs . The symbols represent experimental data points, while the solid lines are fits to an Arrhenius law. The inset shows clearly that deviations from Arrhenius behavior are more pronounced in cesium borate glasses as compared to lithium borate glasses (for a given alkali oxide content).

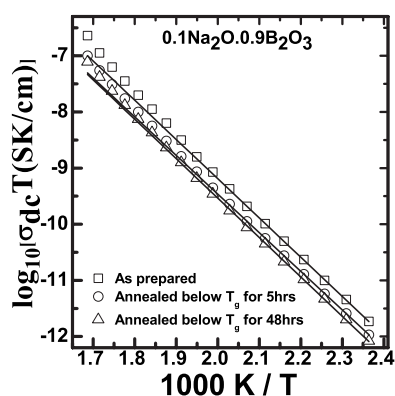


FIG. 4. Arrhenius plot of the dc conductivity (multiplied by the temperature) of a 0.1 Na₂O·0.9 B₂O₃ glass sample with different thermal histories. The symbols represent experimental data points, while the solid lines are fits to an Arrhenius law.

that in the present investigation we did not apply very high quenching rates (like those used for the NMR measurements,^{6,11} since a high quenching rate leads to cracking of the sample). On the other hand, the glass sample annealed 30 K below its glass transition temperature [$T_g = 658$ K] for 48 h shows Arrhenius behavior up to 550 K, which is slightly higher than for the other two samples. Thus the recovery of Arrhenius behavior is enhanced with increasing annealing temperature and time. The same qualitative behavior was observed for a 0.30 Na₂O·0.70 B₂O₃ glass, see Fig. 5. The as-prepared glass shows slight deviations from Arrhenius behavior at higher temperatures, while the glass annealed for 48 h shows Arrhenius behavior over the entire temperature range.

In the following, we discuss the origin of the observed non-Arrhenius behavior and its close correlation to glass structure. In many fast ion conducting glasses, a non-Arrhenius behavior with a negative curvature is found.¹⁵ Recently, such a negative curvature has been reported for potassium silicate glasses, and it has been shown that recovery of Arrhenius behavior is facilitated by annealing processes

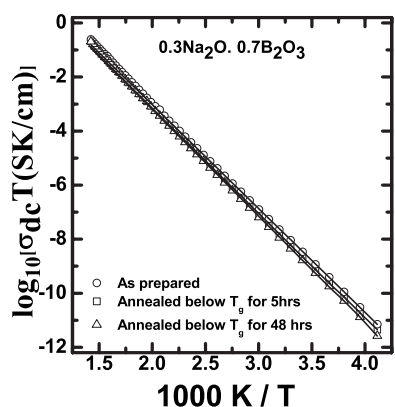


FIG. 5. Arrhenius plot of the dc conductivity (multiplied by the temperature) of a 0.3 Na₂O·0.7 B₂O₃ glass sample with different thermal histories. The symbols represent experimental data points, while the solid lines are fits to an Arrhenius law.

leading to a densification of the glasses.¹⁶ In contrast, it seems that the positive curvature found in this study is a special feature of borate glasses, which is related to their structural peculiarities.

In situ high-temperature NMR and Raman investigations on alkali borate and borosilicate glasses indicate that both raising the temperature and increasing the alkali oxide concentration have a similar effect on the structure, namely the transformation of BO₄ to BO₃+NBO is favored.^{6,11,17} For instance, in a borate glass with 10 mol % Na₂O, the ratio of BO₃/BO₄ is about 7.3% at room temperature and increases to about 14% near T_g . Just above T_g , the ratio becomes nearly 95%. In contrast, in a glass with 30 mol % Na₂O, no such variation of the BO₃/BO₄ ratio with temperature has been found.⁶ Furthermore, it has been shown that the activation enthalpy for this transformation increases with increasing alkali oxide content.¹⁸ Thus at low alkali oxide contents, the temperature-dependent equilibrium between the different boron coordinations can be easily established at different temperatures, while at high alkali oxide contents, the slow transformation rate leads to a more or less temperature-independent boron coordination.

In what way do these structural peculiarities influence the ion transport? Recently, several theoretical groups have investigated ion transport mechanisms in glasses by means of molecular dynamics simulations and have found that only few empty sites for the ions exist.¹⁹ This bears an analogy to the existence of a small number of vacancies in crystalline materials. Therefore a “vacancylike transport mechanism” in glass has been postulated.¹⁹ One of the present authors has used this concept to explain the non-Arrhenius behavior in fast ion conducting glasses.²⁰ In this case, the observed negative curvature was attributed to a temperature-dependent number of empty ionic sites. At low temperatures, the number of empty sites increases with temperature, while at higher temperatures, the number becomes constant. This assumption was supported by deviations from Summerfield scaling in the frequency-dependent conductivity spectra.²⁰

In contrast to fast ion conducting systems, alkali borate glasses exhibit a positive curvature. In the framework of the vacancylike transport concept, this implies a temperature-independent number of empty sites at low temperatures and an increase of the number of empty sites at higher temperatures. The reason for this creation of additional sites at high temperatures could be the structural conversion of BO₄ to BO₃ leading to an increasing number of NBO. An increasing number of NBO implies a depolymerization of the borate network and a more open network structure. Thus it seems plausible that this type of structural conversion leads to more ionic sites in the glass network.

We note that this assumption can also explain an increase of the Haven ratio with temperature as found for rubidium borate glasses.¹³ A small number of empty sites at low temperatures leads to highly correlated movements of the ions and thus to a low Haven ratio. When at higher temperatures more empty sites are created, the correlations between the movements of different ions become weaker and the Haven ratio increases.

In summary, we have shown that the dc ionic conductivity of alkali borate glasses deviates from Arrhenius behavior

with a positive curvature of the data in an Arrhenius plot. The pronunciation of the non-Arrhenius behavior depends on the alkali oxide content, thermal history, and type of alkali ion. By postulating a temperature-dependent number of empty ionic sites and a vacancylike transport mechanism, we provide an explanation for the non-Arrhenius behavior as well as for a temperature-dependent Haven ratio. For drawing a quantitative comparison between structural peculiari-

ties and ion transport properties, more thermodynamic and kinetic data on BO_3/BO_4 conversions at different alkali oxide contents would be desirable.

We acknowledge David Laughman for critically reading the manuscript. Financial support by Sonderforschungsbereich 458 of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

*Present address: Max-Planck Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany.

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