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# STRUCTURE AND $Na^+$ TRANSPORT IN BOROSILICATE GLASSES WITH A HIGH CONTENT OF $Na_2O$ ($\geqq$ 10 mol%) — STUDIED BY $^{22}Na$ TRACER DIFFUSION AND CONDUCTIVITY MEASUREMENTS

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The energies $E_{A,D}$ and $E_{A,\sigma}$ increase with decreasing $Na_2O$ content in the glasses, $E_{A,D} \geqq E_{A,\sigma}$. The energy $E_{A,D}$ corresponds to the movement of the individual ions ($^{22}Na$), influenced by the structure of the glass network. The energy rises with increasing connectivity $CN$, but shows a distinct sensitivity to structural units with NBO. No comparable effects are observable for $E_{A,\sigma}$. The value of $E_{A,\sigma}$ is a biunique function of $CN$. The conductivity is relatively insensitive to structure due to a dominant influence of a cation—cation interaction, depending on the $Na^+$ density $c_{Na}$.

## I. INTRODUCTION

Oxide glasses with high content of alkali oxide are important materials for solid-state electrolyte systems and for ion-exchange techniques generating structures with a modified refractive index for the integrated optics. In glassy solids of the system $Na_2O—B_2O_3—SiO_2$ the network modifier oxide $Na_2O$ simultaneously causes changes in the $Na^+$ density (concentration $c_{Na}$) and in the network structure also. The charge of the $Na^+$ ions can be compensated either by nonbridging oxygen (NBO) from structural units like $SiO_{3/2}O^-$ and $BO_{2/2}O^-$ or by the charge distributed in larger groups without NBO such like $BO_{4/2}^-$. The aim of the present investigation consists in an attempt to separate the specific influence of the network structure and of $Na^+$ density on the ionic transport. Fig. 1 indicates the chemical composition of the glasses. All substitution rows start in the disilicate glass NO ($Na_2O \times 2SiO_2$) with a layer-like structure (connectivity CN = 2). The value of CN can be estimated approximately by

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$CN = 3 - c_{NBO}/c_{NF}$ for these compositions with a low $B_2O_3$ content ($c_{NBO}$ is deduced from [1], $c_{NF}$ represents the concentration of former cations of the network; Si, B).

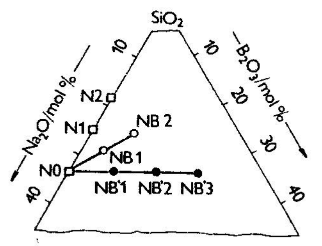


Fig. 1.

## II. EXPERIMENTAL

The $Na^+$ transport was characterized by (1) $^{22}Na$ tracer diffusion studies ($D^*$ self-diffusion, $\gamma$ residual activity technique, $50 \leqq A \leqq 100$ kBq) and by (2) conductivity measurements ($\sigma_{dc}$ from impedance spectroscopy, $10^{-3} \leqq f \leqq 10^5$ Hz). The ARRHENIUS parameters ($E_{A,D}$, $D_0$ and $E_{A,\sigma}$, $\sigma_0$) were calculated from the experimental data corresponding to eq. (1a, b).

$$D^* = D_0 \exp(-E_{A,D}/RT) \quad (1a)$$

$$\sigma = \sigma_0 \exp(-E_{A,\sigma}/RT) \quad (1b)$$

A comparison of these values $D^*$ and $\sigma$ is possible in the concept of the HAVEN ratio $H_R$ [2] (eq. 2).

$$H_R = D^*/D_\sigma \quad (2)$$

with

$$D_\sigma = \sigma(kT/c_{Na}q^2).$$

## III. RESULTS AND DISCUSSION

The ARRHENIUS plot (lg $D^*$ or lg $\sigma$ vs $1/T$) of the measured data gives straight lines for all glasses indicating defined activation energies according to eq. (1a) and (1b), resp. (see also [3]). The energies $E_{A,D}$ and $E_{A,\sigma}$ increase with decreasing $Na_2O$ content in the glasses. However, for every glass we find $E_{A,D} \geqq E_{A,\sigma}$. The HAVEN ratio is in the range of $0.20 \leqq H_R \leqq 0.45$ (300—450°C). $H_R$ increases with temperature.

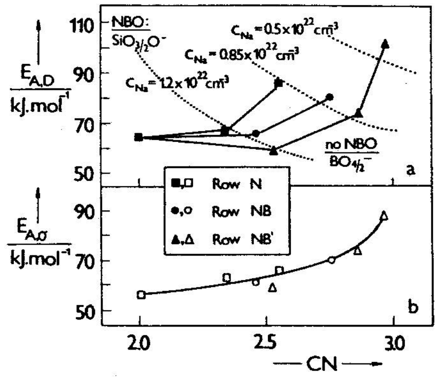


Fig. 2.

Fig. 2 represents the dependence of $E_{A,D}$ and $E_{A,\sigma}$ on the connectivity $CN$ of the glass networks. From the tracer diffusion experiments (Fig. 2a) the energy $E_{A,D}$ is obtained corresponding to the movement of the individual ions ($^{22}Na$), influenced by the structure of the glass network. $E_{A,D}$ rises with increasing connectivity $CN$, but shows a distinct sensitivity to structural units with NBO. In this way, at the lines with constant $Na^+$ densities $c_{Na}$ (...) $E_{A,D}$ drops for the transition from $SiO_{3/2}O^-$ to $BO_{4/2}$ groups. This result demonstrates the enlarged interaction of $Na^+$ with NBO. No comparable effects are observable in Fig. 2b. The value of $E_{A,\sigma}$ is a biunique function of $CN$. In conductivity measurements, the collective displacement of untagged ions ($Na^+$) is determined. The conductivity is relatively insensitive to structure, because there is a dominant influence of a cation—cation interaction, depending on the $Na^+$ density $c_{Na}$ in these solid electrolyte systems with $c_{Na} \gtrsim 0.5 \times 10^{22}$ $Na^+/cm^3$. The present interpretation is in accordance with the recent results of the HAVEN ratio obtained from diffusion studies in an electric field (CHEMLA-experiment) with a new experimental arrangement [4].



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### СТРУКТУРА И $Na^+$ ТРАНСПОРТ В БОРОСИЛИКАТНЫХ СТЕКЛАХ С ВЫСОКИМ СОДЕРЖАНИЕМ $Na_2O$ ($\geqq$ 10 mol%) — ИССЛЕДОВАНИЕ ПРИ ПОМОЩИ $^{22}Na$ ИНДИКАТОРНОЙ ДИФФУЗИИ И ИЗМЕРЕНИЙ ПРОВОДИМОСТИ


Энергии $E_{A,D}$ и $E_{A,\sigma}$ возрастают с уменьшением содержания $Na_2O$ в стеклах, $E_{A,D} \geqslant E_{A,\sigma}$. Энергиа $E_{A,D}$ соответствует движению индивидуальных ионов ($^{22}Na$), обусловленным структурой стекла. Энергиа увеличивается с нарастанием связности $CN$, но показывает различную чувствительность к структуральным единицам с NBO. Никаких сравнимых эффектов не наблюдается для $E_{A,\sigma}$. Значение $E_{A,\sigma}$ является однозначной функцией $CN$. Проводимость является относительно нечувствительной по отношению к структуре благодаря доминантному влиянию катион—катионного взаимодействия, зависящего от $Na^+$ плотности $c_{Na}$.