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# Properties of heat treated sodium alkali borosilicate glasses

E. Rysiakiewicz-Pasek

Institute of Physics, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland.

The electrical properties of sodium borosilicate glasses after heat treatments at different temperatures and different time were investigated. The glasses proved to be phase separated. The dc electrical conductivity measurements were performed to obtain the structure of heated glasses.

## 1. Introduction

Alkali borosilicate glasses are the initial material for production of porous glasses [1], [2]. After heat treatment phase separation occurs in these glasses. In initially homogeneous glass, both sodium-borate rich and silica rich phasees exist.

Depending on heat treatment two possibilities may occur:

1. Both phases are continuous and interconnected.

2. The glass contains one continuous phase with more or less spherical inclusion of another phase.

The volume of each of the phases considerably influences the type of forming phase. If the volume of one of the phases does not exceed 15–20% of the entire sample, this phase almost always exist in the form of droplets. The closer is the volume of the phases to 50% of the entire sample, the greater is the probability of the formation of two phases with continuous structure.

To obtain porous glasses, the alkali borosilicate glasses were immersed in acid solution in order to extract the alkali-borate rich phase. To get a good quality glass both phases have to be continuous and interconnected and the silica rich phase should be obtained with the high content of $SiO_2$.

Te aim of this work is to determine the effect of microstructural features on the alkali ions transport properties. The electrical conductivity of glass before and after heating is related to the transport of alkali ions through the network. The nature of electrical conductivity in the glasses after heat treatment is more complicated in comparison with the unheated glass due to the presence of two phases [1], [3]–[5]. If these phases are interconnected and continuous, the dc conductivity is defined by the highly conducting (alkali-borate rich) phase. If the glass sample consists of small droplets dispersed in a continuous silica rich phase, then the dc conductivity of glass is very small and corresponds well to the dc conductivity of silica glasses with low alkali content.

The electrical measurement can be useful to determine the phase composition. In this paper, we analyse the electrical conductivity of sodium borosilicate glasses measured at different temperatures before and after heat treatments.

## 2. Experimental

The electrical dc conductivity was measured using thermally stimulated polarization current technique. The details of this method and apparatus were described in an earlier paper [6].

The dc conductivity values were obtained from TSP-2 curve [7]. The electrical measurements were performed for the sodium borosilicate glass with the composition (% by weight): 55% $SiO_2$, 33% $B_2O_3$, 10% $Na_2O$, 2% $Al_2O_3$.

The glass samples were thermally treated at 500, 550, 570 and 600° C for different times.

During the electrical measurements the aquadag electrodes (aquadag is a suspension of graphite in water) were applied. The glass dimensions were $10 \times 15 \times 0.5$ mm$^3$. The glasses before TSP measurements were preheated at 373 K for 0.5 h to remove the water absorbed at the surface.

The glass structure was investigated with the scanning electron microscope.

## 3. Results

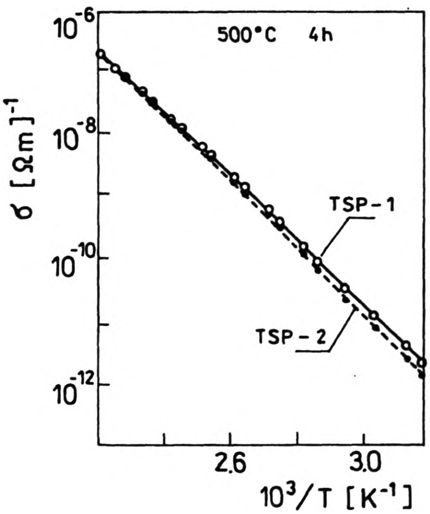
In Figure 1, typical TSP-1 and TSP-2 curves for the glass heated at 500° C for 4 h are presented. In the high temperature range, these curves coincide.

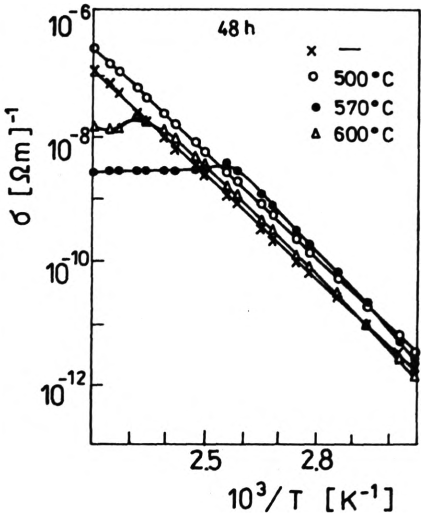
For the same time of heat treatment of glass, the influence of heating on dc conductivity of the investigated glasses is shown in Fig. 2. The heat treatment conditions and the activation energy values for the investigated glasses are presented in the Table. After heating at 500° C the dc conductivity increases in comparison with the initial glass. For the glass submitted to heat treatment at 570° C the dc conductivity initially increases, and at 393 K reaches almost constant value. This curve is identical for the glass heated at 550° C. For the glass heating at 600° C in the temperature range from 313 to 393 K the dc conductivity decreases and from 413 K a constant value is observed.

Table. The activation energy values for investigated glasses ($\Delta E_{dc} = \pm 0.025$ eV)

| $t$ [h] | $T$ [°C] | $E_{dc}$ [eV] | $T$ [°C] | $t$ [h] | $E_{dc}$ [eV] |
|---|---|---|---|---|---|
| 48 | – | 0.96 | 550 | 4 | 1.01 |
| | 500 | 0.98 | | 8 | 0.93 |
| | 570 | 1.08* | | 24 | 0.97 |
| | 600 | 1.02* | | 48 | 1.05* |

* The values of activation energy for the glasses heated at 550, 570 and 600° C for 48 h are determined in the temperature range, where the increase of dc conductivity was observed.




▲
Fig. 1. TSP-1 and TSP-2 curves for the glass heated at 550° C for 4 h

Fig. 2. The dc conductivity dependence on temperature for the glasses heated for 48 h at different temperatures

In Figure 3, the dependencies of dc conductivity on temperature for the glass before and after heat treatment at 550° C for 4, 8, 24 and 48 h are shown. The increase of dc conductivity after heating of initial glass during 4 h is observed. With the increase of the heating time from 4 to 8 h the dc conductivity decrease is observed. After heating the glass for 24 h the dc conductivity insignificantly

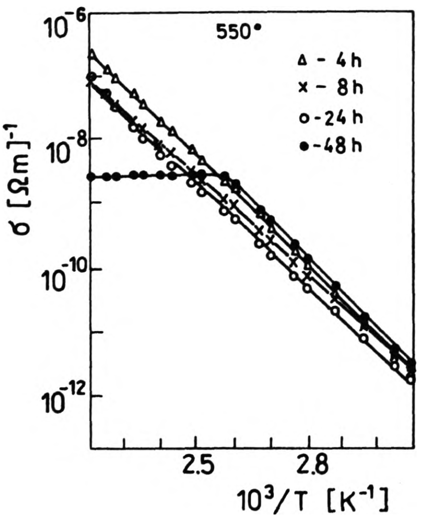



Fig. 3. Depencence of dc conductivity on temperature for the glasses before and after heat treatment at 550° C

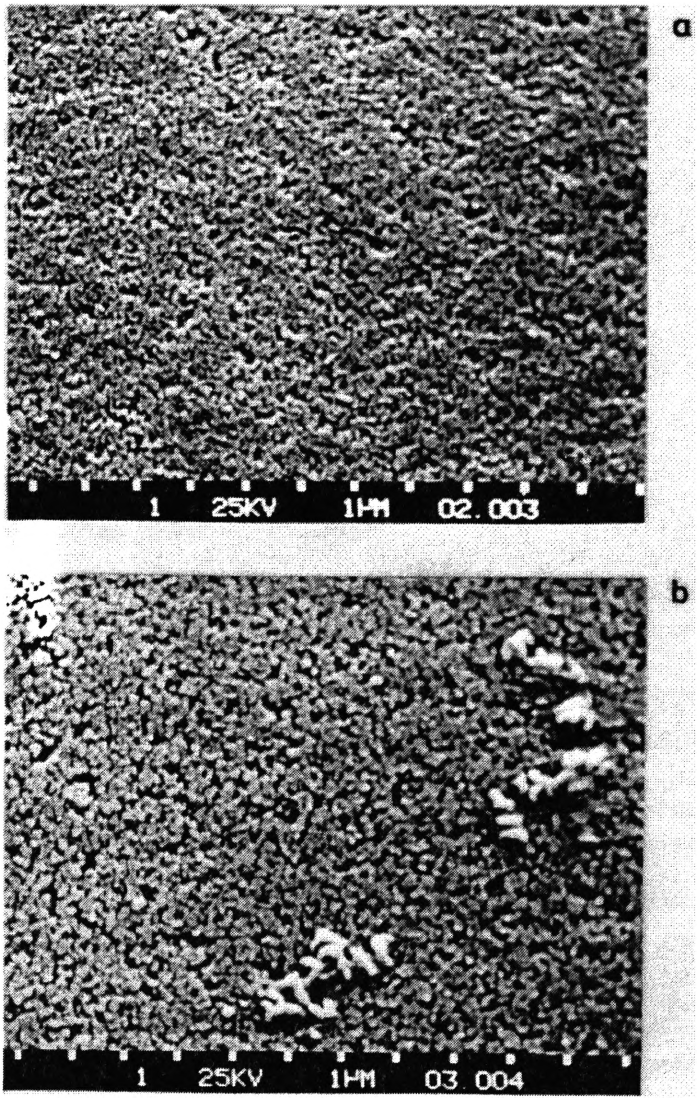



Fig. 4. EM micrographs of investigated glasses (a — heat treatment at 550° C for 4 h, b — heat treatment at 570° C for 48 h)

decreases. For the glasses heated for 48 h, the dc conductivity initially increases up to 388 K and in the temperature range between 388 and 453 K reaches the constant value.

As a result of heat treatment at different temperatures opalescence took place in the investigated glasses. The decrease of optical transmittance was especially pronounced for samples annealed for 48 h at 550–600° C. Depending on temperature the glasses from transparent (the glasses heated at 500° C) become milky. The electron micrographs of investigated glasses are shown in Fig. 4.

## 4. Discussion

The fact that the transmittance decreases strongly implies that inhomogeneities with dimensions comparable to (or exceeding) the wavelength of the visible light are created in the volume of the investigated samples. The changes of dc conductivity can be also attributed to the creation of these inhomogeneities. It is well known that the sodium-borate phase has a significantly higher conductivity compared with the $SiO_2$ phase because of high sodium ion concentrations. We argue that filaments of sodium-borate rich phase form a percolation net [8] responsible for the conductivity of studied specimens. As a result of heat treatments the structure of the percolation cluster is modified. Two processes take place during annealing:

1. Continuous phase separation (creation of new percolation paths).
2. Segregation of already existing sodium-borate phase (the size of regions with increased ion concentration increases as well as the density of corresponding ions).

This explain the nonmonotonous changes of the dc conductivity observed in our experiments. In cases when annealing procedure was carried out at high temperatures and lasted long enough, the regions of high ion concentration were characterized by decreased values of the ion activation energies. A similar situation was revealed and analysed in [9] for the case of ion migration on the walls of pores in the porous $SiO_2$ matrix. The potential wells that correspond to the activation hops of ions are located so close that tunneling between neighbouring sites becomes possible [10]. The supposed structure of conductive filaments and the corresponding equivalent circuit are shown in Fig. 5.

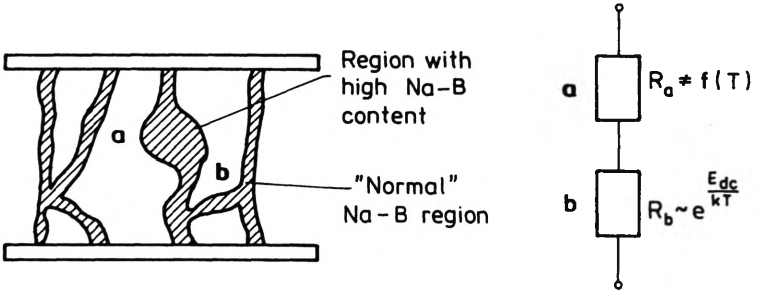



Fig. 5. Schematic diagram of the leakage filament

At low temperature $R_a \ll R_b$ and the total conductivity is limited to $R_b$. When the temperature increases the resistance of high Na – B concentration region, which has no activation dependence on temperature, is such that $R_a \gg R_b$. This explains the saturation of current (Figs. 2 and 3) observed in our experiments in case of long-lasting thermal treatments at high temperatures.

## 5. Conclusions

We have shown both by optical transmittance and electrical measurements that regions with sizes of the order of the visible light wavelength and large concentrations of sodium and boron atoms are created in sodium-borosilicate glasses. A model is proposed which accounts for the observed peculiarities. It follows from this work that the dc conductivity measurements can be effectively used to analyse the structure of sodium borosilicate glasses.

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