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Influence of copper impregnation on the properties of porous glasses

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The properties of porous glasses impregnated with cooper were investigated. The influence of different concentration of cooper on electrical properties of macroporous glasses was determined. The results of measurements of dc conductivity were discussed on the basis of the structure of porous glasses.

1. Introduction

The glass obtained from the $Na_2O-B_2O_3-SiO_2$ system are initial staff for production of porous glasses. During heating two phases – sodium-borate and silica rich – are formed. After leaching the borates in acid solution, pure silica glasses were obtained. For the fabrication of porous glasses the following conditions should be fulfilled:

– both phases should be interconnected and continuous,

– the silica rich phase should contain as much SiO_2 as possible,

– the alkali rich phase must be easily soluble in acid solutions.

The porous glasses have found application in optics, optoelectronics, medicine and biotechnology. They are known as adsorbents of gas, solid catalysts, matrices for hologram recording, optical filters [1]–[5].

The properties of porous glas structure (diameter of pores, pore surface, pore volume, transmission) are very important parameters for obtaining high-quality devices. The structure of porous glasses depends upon the technology parameters (temperature and time of heat treatment, time and temperature of leaching in acid solution). It has been shown that electrical measurements can be useful to determine the properties of porous glasses and the properties of substances inside the pores. Investigations of the structure of the porous glasses before and after impregnation with different substrates are also very important.

In our earlier paper [6], the connection of structure (different sizes of pores) and properties of porous glass impregnated with copper have been shown. The aim of this paper is to analyze the influence of impregnation copper concentration on the properties of the macroporous glasses. The main idea is to employ the extended inner surface of porous glass for the investigations of ion transport on silica surfaces. This is extremely difficult to do by measurements on standard (not porous) samples.

2. Experimental

The porous glasses employed in our experiments were obtained by heat treatment of sodium borosilicate glass (SBN-2) at 650° C for 25 h and subsequent leaching in the acid solution followed by cleaning in the deionized water.

After leaching microporous glasses were formed. During the treatment of microporous glasses by immersing samples into 0.5 N KOH at 300 K for 1 h, the secondary silica was removed from the pores and the increase of their diameters and volumes was observed. The measurements of macropore diameter, pore surface and pore volume were made by the absorption-desorption of nitrogen at the temperature of liquid nitrogen. For the obtained macroporous glasses the pores dimensions are 170 – 210 Å, the pore surface equals to 46 – 55 m^2/g and the volume of pores reaches 0.24 cc/g.

The macroporous glasses were then immersed into the solution of copper nitrate (0.1, 0.4, 0.8, 1.0 mol/l) for 21 h. The concentrations of the introduced copper obtained by chemical analysis are presented in the Table. The samples were then dried and immersed in hexamethyldisilizane (HMDS) for 2 h to remove water from the pores.

Table. Activation energy values for measured glasses ($\Delta E_{dc} = \pm 0.025$ eV)

Glass number		Cu [%]	E_{dc} [eV]
$t =$ 21 h	1	0.48	1.03
	2	1.05	0.86
	3	1.90	0.85
	4	2.54	0.75

The dc conductivity was measured using thermally stimulated current technique (TSP) [7]. This method is widely applied as equivalent method to the standard method. In TSP measurements, first, the sample is heated from the low temperature with the external electric field applied ($E_p = 1 \times 10^5$ V/m). During heating TSP-1 curve is registered. Then, the sample is rapidly cooled with the external field and is heated again (TSP-2).

The dc conductivity values are determined from TSP-2 curve. In high temperature range both these curves (TSP-1 and TSP-2) coincide.

The activation energy for dc conductivity is calculated from the slope of $\log \sigma$ *vs.* $1/T$ from the equation

$$\sigma = \sigma_0 \exp(-E_{dc}/kT)$$

where: σ – conductivity, σ_0 – preexponential factor, E_{dc} – activation energy for dc conductivity, T – temperature, k – Boltzmann's constant.

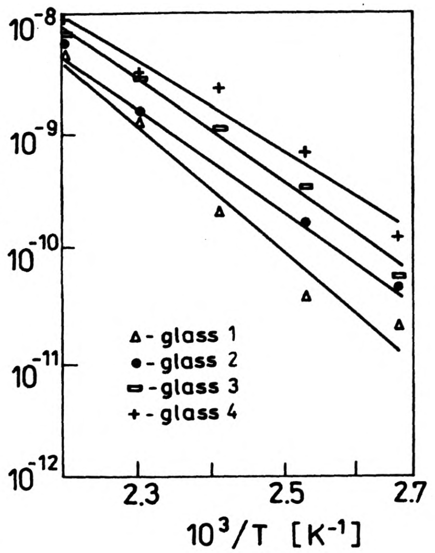
The aquadag electrodes (aquadag is a suspension of graphite in water) were used in TSP measurements.

Before the TSP measurements glasses with dimensions of $10 \times 15 \times 0.5$ mm^3 were preheated at 373 K for 0.5 h to remove water from the surface of glass.

3. Results

The dc electrical conductivity dependences on temperature for the macroporous glasses after impregnation with copper are shown in Fig. 1. The obtained activation energy values E_{dc} are presented in the Table.

The dc conductivity as a function of copper concentration for the investigated glasses is presented in Fig. 2. It is evident that at the temperature range between 393 and 453 K, the dc conductivity increases with increase of copper concentration.



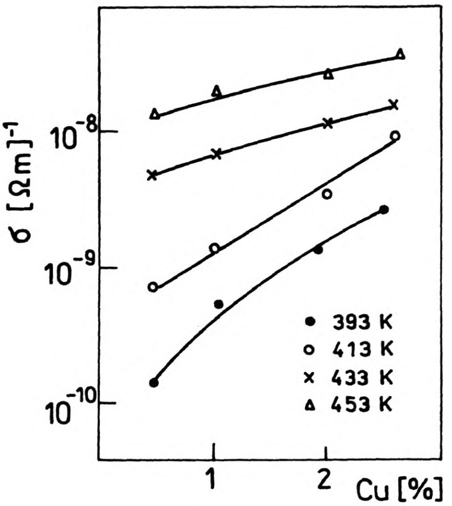


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Fig. 1. The dc conductivity dependence on temperature for the glasses after impregnation with copper

Fig. 2. The dc conductivity dependence on copper concentration

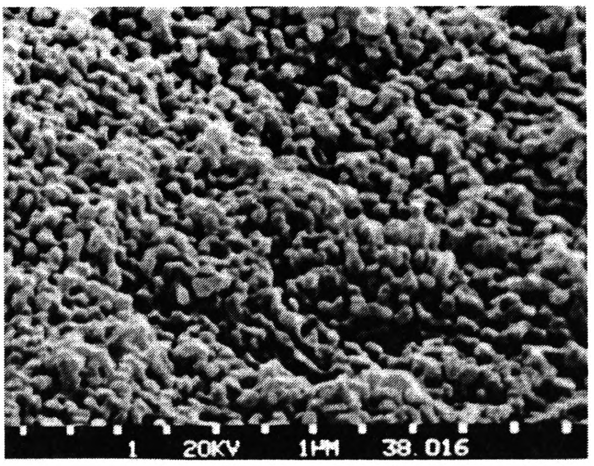

Fig. 3. Photograph of "pure" macroporous glass made by scanning electron microscope

The structure of "pure" macroporous glass obtained from electron microscope is presented in Fig. 3.

4. Discussion

The properties of substance impregnated into the pores are dependent on the structure of glasses. The microporous glass obtained from initial glass after leaching in acid solution contains "secondary" silica on the surface of pores. The treatment of microporous glass in the alkali solution results in the removal of secondary silica. The structure of macroporous glass is related to the structure of the initial phase-separated glass. The sizes and volume of pores increase. The dc conductivity of pure porous glass at 373–473 K is less than 10^{-11} [Ohm·m]$^{-1}$. After impregnation with copper, the dc conductivity increases (Fig. 2).

The surfaces of pores, as it is seen from Fig. 3, are rather smooth. The sizes of voids are longer than the mean distance between Cu atoms even for small concentrations. In this case

$$d = \sqrt{\frac{Sm}{A\alpha}} \sim 10\ \text{Å} \tag{2}$$

where : α – concentration of Cu atoms, S – pore surface, A – Avogadro number, m – molecular mass of Cu.

To maintain charge neutrality of the sample, an electron captured at SiO_2 surface must reside near each Cu atom. The probable candidates for the electronic traps are Si–OH bonds [8].

For high α values the potentials of the neighbouring Cu atoms intersect resulting in the significant decrease of the activation energy [9].

The mobilities of Cu ions can be easily estimated from measured values of dc conductivity

$$\mu = \frac{\sigma m}{\alpha q A \rho} \tag{3}$$

where: ρ – density of porous glass, which at at 373 K is of the order of 10^{-17} m^2/Vs (for maximum Cu concentration of about 2.5%).

The mobility has an activation dependence on temperature with the activation energy given in the Table.

5. Conclusions

A method of Cu ion mobility evaluation on the walls of voids in porous glasses based on TSP measurements of Cu doped glasses is proposed. The value of Cu mobility was estimated on the basis of surface ionic transport measurements.

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