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# Effect of the microstructure on transport properties of doped SLS glasses

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Results of thermally stimulated polarisation current measurements and transmission electron microscopy investigations of copper-exchanged soda lime silicate glasses are presented. During the ion exchange procedure, sodium ions are partially substituted by copper. It has been stated that, besides the formation of copper and copper oxide, the joint effect of chemical and thermal treatment is the modification of matrix morphology. Thus, the induced modification of transport properties could be related to mobility changes for $Na^+$ charge carriers.

Key words: *soda lime silicate glass; conductivity; ion exchange*

## 1. Introduction

Oxide glasses containing small particles of transiition metals can be used as resonant-type non-linear optical materials for photonic devices [1]. Ion implantation and ion exchange techniques are usually used to introduce metal ions into glass networks. Subsequent thermal treatment in an inert or reducing atmosphere results in the formation of metallic atoms and colloidal particles. Preliminary studies of copper-doped soda lime silicate glasses (SLSG) have shown that the thermally stimulated depolarisation current (TSDC) spectra of these materials are sensitive to ion exchange parameters and post-exchange thermal treatment [2].

To obtain a deeper insight into these phenomena, thermally stimulated polarisation (TSP) and depolarisation (TSD) current measurements and transmission electron microscope (TEM) observations were performed for commercial SLSG subject to chemical and thermal treatment.

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## 2. Experimental

The composition of the commercial multicomponent glass (determined by EDX) was as follows (in mole %): $SiO_2$ – 74, $Na_2O$ – 13, CaO – 6.4, MgO – 4.5 and $Al_2O_3$ – 1.4. Ion exchange was performed in an air atmosphere by dipping the glass plates into molten $Cu_2Cl_2$ at 900 K for various time periods. Then the samples were annealed in a stream of dry hydrogen at 773 K for 5 hours under atmospheric pressure.

Measurements of thermally stimulated polarisation (TSP1 and TSP2) and thermally stimulated depolarisation (TSD) currents were performed in vacuum [3] as a function of temperature from 150 to 450 K. For the TSP runs, the samples were first cooled to 150 K, and then heated at a constant rate with a polarising field of 400 V/cm ON. The polarisation current (TSP1) was recorded as a function of temperature. After the first run, the sample was cooled again to 150 K with the electric field ON, reheated and the TSP2 current was measured. After TSP2, the sample was cooled to 150 K for the third time, short-circuited, and reheated while the TSD current was recorded with the external electric field OFF.

A Philips scanning microscope (SEM 515) with a microanalyser (EDX 9800) was used to determine the composition of the SLS glasses and the concentration of Cu ions as a function of the distance from the exchanged surface. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were used to study the morphology of the exchanged layer by means of a PHILIPS CM 20 microscope. For these performances, shadowed and extraction replicas were prepared.

## 3. Results and discussion

Figure 1 shows the dependence of Cu and Na ion concentration on the distance from the glass surface as a function of the exchange time at 900 K. It can be seen that for exchange times longer than 2 h, the penetration profile has a step-like character with a constant Cu concentration. The thickness of the exchanged layer reaches a maximum value of about 80 μm. For shorter times, the amount of substituted Na ions is smaller. During reduction, performed at 773 K, sodium ions move towards the sample surface, while copper enters deeper into the glass and the original step-like profile becomes flatter [4]. The hydrogenation of the exchanged samples modifies the valence state of the copper ions and induces the formation of copper colloids.

For all samples, TSP1, TSP2, and TSD measurements were performed. In TSP1, two thermally stimulated polarisation bands are accompanied by a high temperature component (see Fig. 2). These two bands are better seen in the TSD spectrum, whose behaviour has been already described by Suszynska et al. [2]. In TSP2, only the high temperature component appears. Since TSP1 = TSP2 + TSD, the polarisation and transport properties of the investigated glasses can be separated. Moreover, TSP2 data can be used to calculate the dc conductivity and activation energy of the detected charge transport.

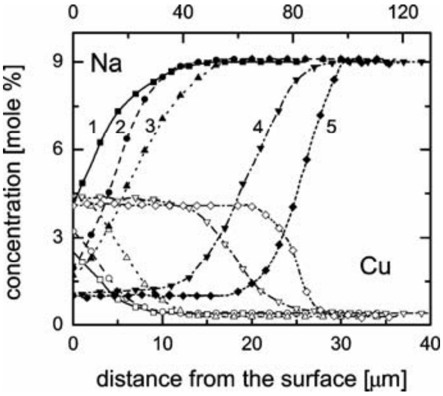

Fig. 1. Penetration profiles for Na (solid) and Cu (open symbols) ions in the surface layer of samples ion exchanged for 10 min (1), 1 h (2), 2 h (3), 6 h (4), and 24 h (5). The upper scale is used for curve 5 (open and solid diamonds)

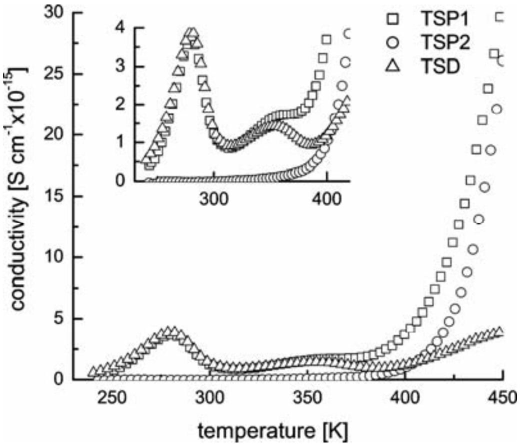

Fig. 2. An example of thermally stimulated polarisation (TSP1 and TSP2) and depolarisation (TSD) spectra (a hydrogenated sample ion-exchanged for 24 h)

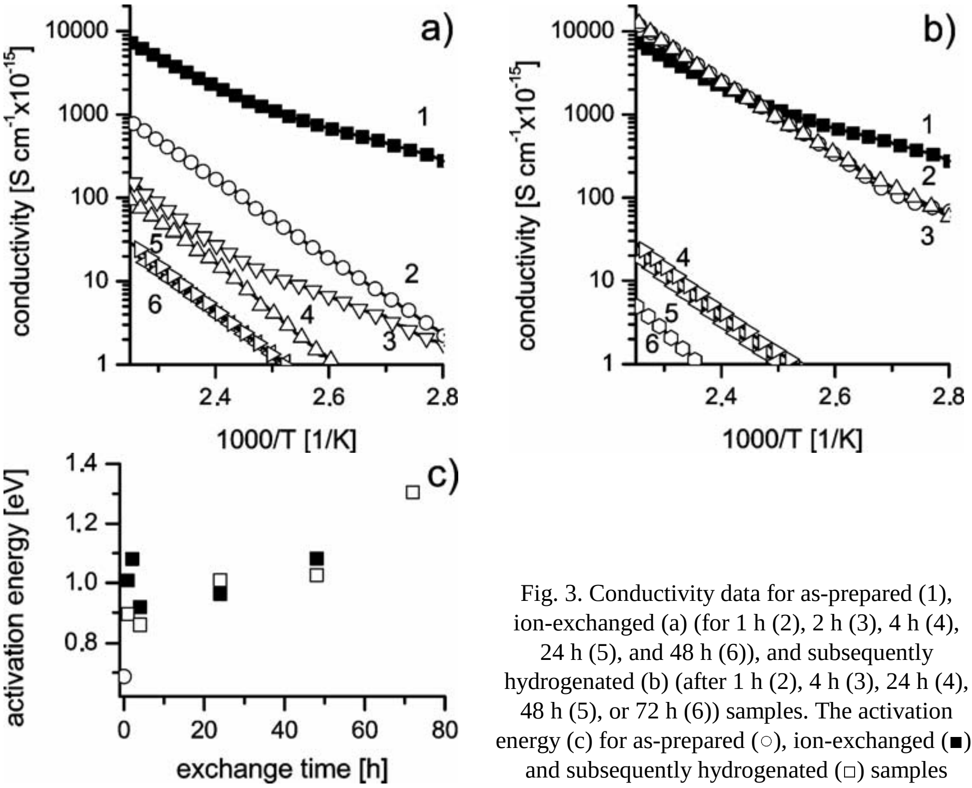

Fig. 3. Conductivity data for as-prepared (1), ion-exchanged (a) (for 1 h (2), 2 h (3), 4 h (4), 24 h (5), and 48 h (6)), and subsequently hydrogenated (b) (after 1 h (2), 4 h (3), 24 h (4), 48 h (5), or 72 h (6)) samples. The activation energy (c) for as-prepared (○), ion-exchanged (■), and subsequently hydrogenated (□) samples

It has been found that the annealing of as-prepared samples at 900 K for several hours and their hydrogenation does not modify the charge-transport properties of the investigated glasses. The dc conductivities and activation energies of such samples are similar to those obtained for as-prepared samples. On the other hand, for samples exchanged with copper, the dc conductivity monotonously decreases with increasing exchange time; for instance, a decrease of about three orders of magnitude was detected for the sample exchanged for 48 h (Fig. 3a). The decrease in the number and/or mobility of the main charge carriers (i.e. the $Na^+$ ions, [5]) might be responsible for the observed changes. Also, the hydrogenation of the samples modifies their conductivities. Namely, for hydrogenated samples previously exchanged shorter than 4 h, the recorded currents increase up to the value characteristic of the as prepared samples (Fig. 3b). For samples exchanged longer, the conductivity is similar to that obtained for glass before hydrogenation.

Figure 3c shows the behaviour of the calculated activation energy. It has been stated that the incorporation of copper results in an increase of the activation energy from 0.69 eV (that of an untreated sample) to nearly 1 eV and 1.1 eV for samples exchanged for 1 h and 2 h, respectively. For longer exchange times and for all hydrogenated samples, the activation energy increases nearly linearly with the exchange time. It seems probable that the joint effect of copper and annealing temperature either induces a new type of matrix morphology or modifies the existing one. The different mobilities of the main charge carriers inside the related matrix species affect the conductivity data. This hypothesis has been confirmed by direct TEM observations.

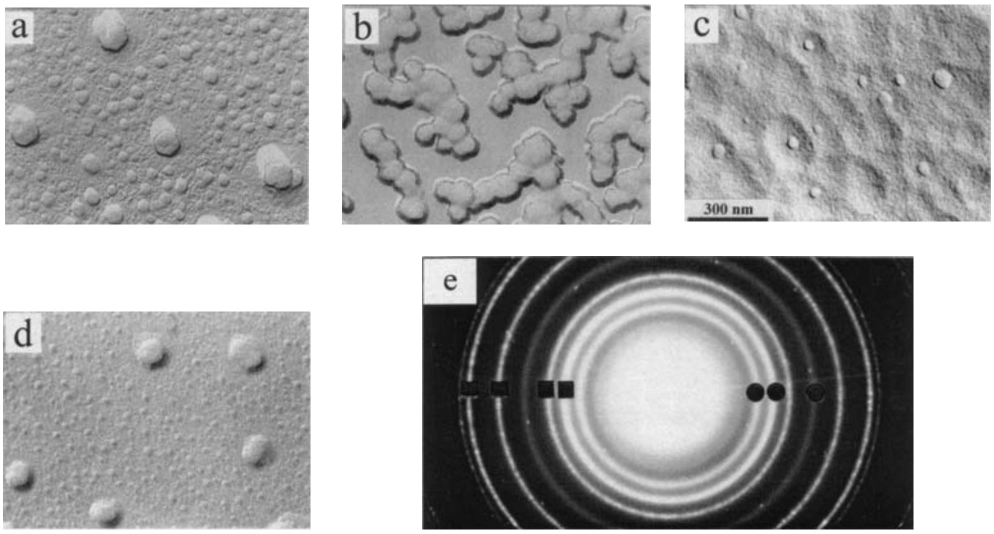

Fig. 4. TEM micrographs of the SLS glass surface of exchanged (*a* = 10 min, *b* = 1 h, *c* = 6 h, *d* = 24 h) and hydrogenated samples. The electron diffraction patterns (e) evidence the presence of Cu (■) and $Cu_2O$ (●) crystallites

Changing matrix morphology with the exchange time is shown in Fig 4a–d; Figure 4e shows the presence of copper and copper oxide colloids. Phase separation, a highly connected structure, and secondary phase separation were observed. Unfortunately, the identification of these occlusions was not possible, because a corresponding crystalline form was not detected. Assuming that the originally separated phase is the $Na_2O$-rich one (as observed for silver doped SLS glass of a similar composition [6]), the incorporation of copper supposedly modifies the existing phase into another with continuously changing morphology and/or composition. These structural modifications affect the mobility of the charge carries and the resulting dc conductivity. The changed mobility of the charge carriers in the copper-rich layer may, however, result in the formation of a space charge between the exchanged and copper free part of the matrix, changing the internal electric field. Future investigations are necessary here.

## 4. Conclusions

dc electric conductivity measurements and TEM observations have been used to show the effect of copper incorporation on SLS glass microstructure. It has been shown that copper dispersed in the glass matrix in the form of ions, atoms, and colloidal particles of copper and copper oxide affect the conductivity in an indirect way by changing the quantity and mobility of the main charge carriers.

**Acknowledgement**

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## References

[1] Hache F., Richard D., Flytzanis C., Kreibig U., Appl. Phys., A 47 (1988), 347.
[2] Suszyńska M., Macalik B., Krajczyk L., Capelletti R., J. Alloys Compounds, 378 (2004), 155.
[3] Gubański A., Macalik B., Bull. Acad. Pol. Sci., Ser. Tech., 35 (1987), 537.
[4] Macalik B., Krajczyk L., Okal J., Morawska-Kowal T., Nierzewski K., Suszyńska M., Rad. Effect Defects Solids, (2002), 887.
[5] Owen A.E., [in:] J.E. Burke (Ed.), *Progress in Ceramic Science*, vol. 3, Pergamon Press, New York, 1963, p. 77.
[6] Suszyńska M., Krajczyk L., Capelletti R., Baraldi A., Berg K.-J., J. Non-Cryst. Solids., 315 (2003), 114.

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