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Effect of short time reduction on electrical properties of bismuth-silicate glasses

KONRAD TRZEBIATOWSKI, JOANNA GACKOWSKA, WITOLD LIZAK, LEON MURAWSKI

Faculty of Applied Physics and Mathematics, Gdańsk University of Technology,
Narutowicza 11/12, 80-952 Gdańsk, Poland

We have investigated the effect of short time reduction on the electrical conductivity of the $70\,SiO_2–25\,Bi_2O_3–5\,K_2O$ (mol%) bismuth silicate glasses. During a short time heat treatment in hydrogen (about 5 min at 375°C) the surface conductivity increases several orders of magnitude. It is suggested that in these samples the charge carriers transport is an electron hopping between localized states in defected silica films containing small Bi clusters. The influence of bismuth granules on conductivity is visible in the second stage of reduction, which takes place after longer than 4 h reduction time. In this case the conductivity exhibits typical of granular metals behaviour.

Keywords: bismuth-silicate glass, electrical conductivity, reduction in hydrogen.

1. Introduction

Reduced lead or bismuth containing glasses have wide use in electronic devices requiring a controlled high resistivity together with the modification of glass properties. In particular, they are used extensively for manufacturing channel electron multipliers [1]. Generally, a conventional lead-silicate glass with high amount of PbO or Bi_2O_3 may be treated in hydrogen at a raised temperature (300–500°C) for a few hours to produce an electronic conducting layer of the surface. There are large differences in reduction process of the binary SiO_2-PbO and SiO_2-Bi_2O_3 glasses. Reduced lead silicate glasses contain rather large Pb grains that are separated at large distances. Hence, the surface conductivity is low, usually below 10^{-11} S at room temperature. Contrary to the lead-silicate glasses, the bismuth-silicate glass exhibits high surface conductivity which can be controlled by time or temperature of reduction process [2, 3]. In order to understand the mechanism of Bi granules formation, it is important to investigate the early stage of reduction process. In the present contribution we have studied the effect of short time reduction on electrical conductivity of the glass containing (in mol%) $25\,Bi_2O_3–70\,SiO_2–5\,K_2O$.

2. Experimental

Glass of nominal composition (in mol%) $25Bi_2O_3$–$70SiO_2$–$5K_2O$ was synthesized as follows. The mixture of powdered SiO_2, KNO_3 and bismuth nitrate $4BiNO_3(OH)_2$–$BiO(OH)$ placed in a platinum crucible was heated in an electric furnace and decomposed at 800°C. After decomposition the mixture was ground again and melted for about 1 hour in the platinum crucible in air at 1200°C. Melted glass was homogenized by mechanical stirring and then quenched by pouring onto a steel plate. For electrical conductivity measurements the rods of approximately 1.5 mm in diameter and 3.5 mm long were cut and two wires were connected to the ends of the rod. The measurements were performed in a special silica glass chamber with controlled atmosphere. For high temperature measurements the chamber was inserted into the small furnace. The conductivity was measured in the range of temperature from 300 to 700 K using Keithley 6485 picoammeter with automatic data collection and automatic temperature regulation. The equipment enables observation of the conductivity changes during the reduction as well as the measurements of the temperature dependence of the electrical conductivity. Low temperature measurements from 4.2 K up to room temperature were carried out in helium cryostat using 4 terminal method. The measurements were performed at constant heating rate of 0.1 K/min and 1 K/min at low and high temperature, respectively.

The surface conductivity of the samples has been calculated from equation $\sigma_{\square} = R^{-1}d/l$, where R is the resistance of the sample, d is the distance between the electrodes and l is their length.

The glass and its reduced surface layer were examined by X-ray diffraction analysis with the use of Philips X'Pert diffractometer system. Qualitative analysis of diffraction spectra was carried out with ICDD PDF database.

3. Results and discussion

The reduction process in bismuth silicate glass was investigated by isothermal measurements of dc conductivity. The plot of surface conductivity versus reduction time of the $70SiO_2$–$25Bi_2O_3$–$5K_2O$ sample reduced at 648 K is presented in Fig. 1. We can distinguish two stages of reduction. The first short time reduction takes place up to 5 min. The surface conductivity increases several orders of magnitude. This jump of conductivity is attributed to the reduction of Bi ions, which are located on the top of the surface. In this stage of reduction XRD does not reveal bismuth peaks (Fig. 2). A temperature dependence of conductivity after 10 min reduction during cooling is shown in Fig. 3. The activation energy decreases from 0.35 eV at high temperature range to below 0.1 eV at room temperature. It is suggested that charge carrier transport is an electron hopping between localized states in defected silica films containing small Bi clusters. Bismuth granules start to appear on the surface after longer time of reduction. As it can be seen in Fig. 2 XRD pattern shows bismuth peaks after 80 min reduction. After this time of reduction the agglomeration of Bi atoms into the granules

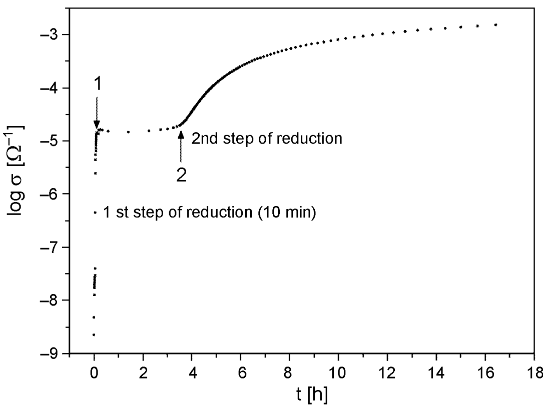

Fig. 1. Time dependence of surface conductivity of the $70SiO_2$–$25Bi_2O_3$–$5K_2O$ glass during heat treatment in hydrogen at 648 K.

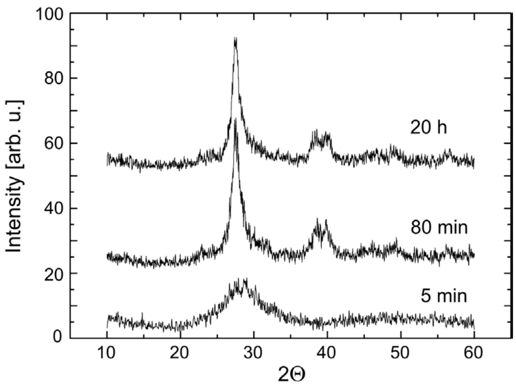

Fig. 2. X-ray diffraction spectra of the samples after different time heat treatment in hydrogen.

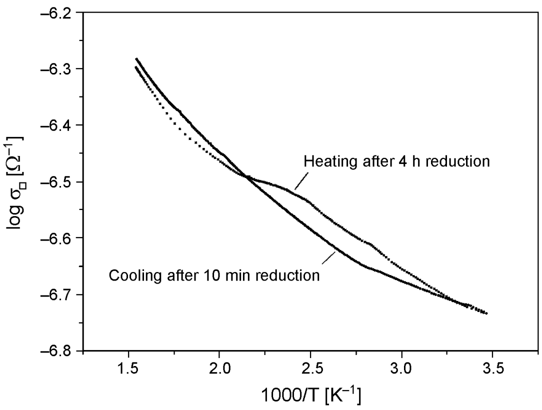

Fig. 3. Temperature dependence of conductivity in $70SiO_2$–$25Bi_2O_3$–$5K_2O$ glass after first step of reduction (10 min) and after 4 h reduction.

does not change the conductivity (see Fig. 1). The conductivity starts to increase during the second stage of reduction, which takes place after longer than 4 h reduction time. Conductivity measurements after 4 h reduction exhibit some changes near 400 K (Fig. 3). This phenomenon is attributed to the melting of nanosized bismuth granules. It is well known that the melting behaviour of nanosized particles is different from that observed in the bulk material. It was shown that the melting point depression is considerably lower by reducing particle size [4]. The melting point for bulk bismuth is 544 K. Figure 4 shows that during cooling the solidification between 419 and 388 K induces a large change in conductivity in the glass reduced during 18 h in hydrogen. The conductivity increases because in solid state the volume of bismuth increases about 3.3%. As shown in our previous paper, it is possible to evaluate the size of Bi

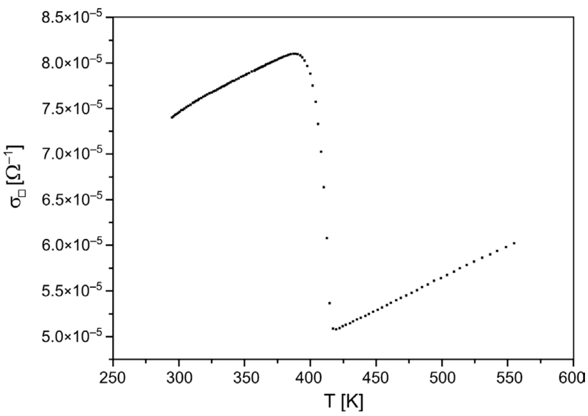

Fig. 4. Influence of bismuth granules solidification on conductivity. The glass was reduced in hydrogen about 18 h at 648 K.

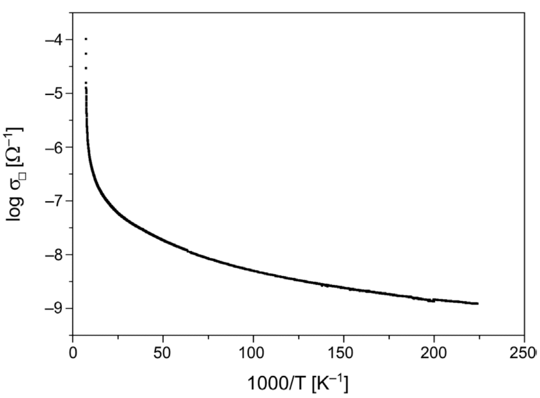

Fig. 5. Temperature dependence of the conductivity of 18 h reduced $70SiO_2$–$25Bi_2O_3$–$5K_2O$ glass.

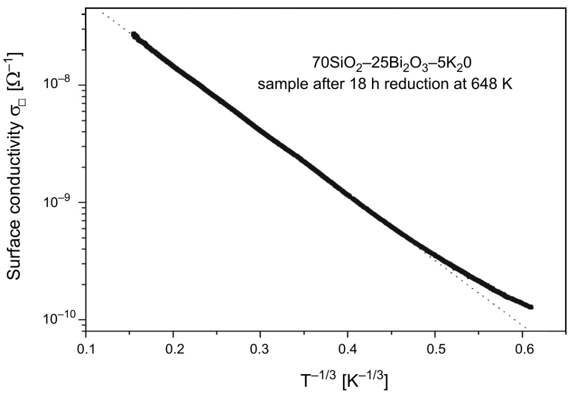

Fig. 6. Plot of surface conductivity versus $T^{-1/3}$ (low temperature measurements: 4.4–300 K).

particles from the change of the melting point [5]. Assuming that nanosized bismuth particles are embedded in the glass matrix, we estimated that their sizes do not exceed 10 nm. However, the result of low temperature measurements of conductivity indicates that a distribution of granule size should be taken into account for conductivity behaviour. The conductivity measurement as a function of temperature in the low temperature range between 4.4 to 300 K shows that the activation energy continuously decreases with decreasing temperature (Fig. 5). This dependence suggests that the Hill and Coutts model [6] can explain the conduction mechanism in this glass. The electrical transport is an electron tunnelling mechanism between metal granules of different sizes. In this model the low-temperature conductivity should obey the law:

$$\sigma(T) = \sigma_0 \exp\left[(-T_0/T)^n\right].$$

Hill and Coutts showed that for a variety of size and distance distributions of metal granules, one may obtain conductivity-temperature dependences in the above form where $1/3 < n < 1$. The exponent n depends on the concentration of granules and temperature. At very low temperatures $n = 1/3$ and then n increases continuously to $n = 1$ in the high temperature range.

As shown in Fig. 6 this relation is fulfilled in the sample reduced during 18 h in hydrogen at 648 K.

4. Conclusions

We have investigated the effect of short time reduction on the electrical conductivity of the $25Bi_2O_3$–$70SiO_2$–$5K_2O$ (mol%) bismuth silicate glasses. During a short time heat treatment in hydrogen the surface conductivity increases several orders of magnitude. It is suggested that in these samples the charge carriers transport is an electron hopping between localized states in defected silica films containing small Bi clusters. The influence of bismuth granules on conductivity is observed in the second stage of reduction, which takes place after longer than 4 h reduction time. In this case the conductivity exhibits typical of granular metals behaviour.

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