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Structure and morphology of hydrogen reduced surface of bismuth germanate and bismuth silicate glasses

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Bismuth nanoclusters embedded in germanate glass matrices and surface layer of bismuth grains have been obtained by thermal treatment in hydrogen atmosphere of $Bi_{0.33}Ge_{0.67}O_{1.84}$ and $Bi_{0.57}Si_{0.43}O_{1.72}$ glasses. A simple two-layer model of reduced glasses, proposed by us on the basis of XRD and AFM studies, explains the evolution of surface layer and electrical properties of the materials during the reduction process.

Keywords: hydrogen reduced glass, X-ray diffraction, AFM, nanostructures.

1. Introduction

Bismuth silicate glasses find a lot of industrial and special applications, *e.g.*, [1], [2]. On the other hand, bismuth germanate glasses are less known and their applications are still rare. Bismuth germanate and bismuth silicate glasses change their physical properties in the course of heat treatment in hydrogen atmosphere. For instance, surface conductivity increases by several orders during appropriate heat treatment. Changes in material properties are directly related to the evolution of the structure and morphology of the glass surface. Annealing in hydrogen reduces Bi^{+3} ions into neutral atoms which subsequently agglomerate into granules on the surface and inside the glass. Only a few works have been devoted to physical properties of non-reduced [3] and reduced [4], [5] bismuth germanate glasses and there still remain many questions about conductivity and structures of these materials. In this paper we present a simple model of the glass subjected to the reduction process.

2. Experiment

Glasses of nominal composition $Bi_{0.33}Ge_{0.67}O_{1.84}$ and $Bi_{0.57}Si_{0.43}O_{1.72}$ were synthesized as follows. Milled mixture of powdered SiO_2 or GeO_2 and Bi nitrate, placed into a platinum crucible, was decomposed at 1000 K for one hour. After the decomposition, the mixture was ground again and submitted to a gradual heating from room temperature to 1500 K. Melted glass was homogenized by mechanical stirring and then quenched by pouring onto a steel plate. Before further treatment the surface of samples was polished and cleaned carefully. The nominal oxygen content in the glass was calculated within the assumption that the original glass has a composition determined by the valence 3+ of Bi and 4+ of Ge.

Reduction process was carried out at 613 K in hydrogen atmosphere. In this paper we present the results obtained for $Bi_{0.33}Ge_{0.67}O_{1.84}$ samples reduced for 0.8 h (G1), 2 h (G2), 7 h (G3), 12 h (G4), 24 h (G5) and 44 h (G6), and also for $Bi_{0.57}Si_{0.43}O_{1.72}$ glass reduced for 0.3 h (S1), 2 h (S2), 5 h (S3) and 24 h (S4).

Surface morphology of reduced samples was tested by means of an air AFM microscope. The glass and its reduced surface layer were examined by X-ray diffraction with the use of Philips X'Pert diffractometer system. Qualitative analysis of diffraction spectra was carried out with ICDD PDF database.

Measurements of sample conductivity were made using the two-terminal method. The measurements were performed during reduction. The surface conductivity of the samples has been calculated from the following equation: $\sigma_{\square} = R^{-1}d/l$, where R is the resistance of sample, d is the distance between the electrodes and l is their length.

3. Results

The plots of surface conductivity versus reduction time of $Bi_{0.33}Ge_{0.67}O_{1.84}$ and $Bi_{0.57}Si_{0.43}O_{1.72}$ samples reduced at 613 K are presented in Fig. 1. It can be seen that reduced bismuth germanate and bismuth silicate glasses have different time dependences. The curve of $Bi_{0.33}Ge_{0.67}O_{1.84}$ presents typical behaviour characteristic of bismuth germanate glasses subjected to the reduction process [6]. First, after some time a rapid, of a few orders of magnitude, increase in the surface conductivity appears. Next, the surface conductivity attains a maximum (about $10^{-6}\ \Omega^{-1}$) and decreases to a minimum. Further reduction causes an increase in conductivity of a few orders.

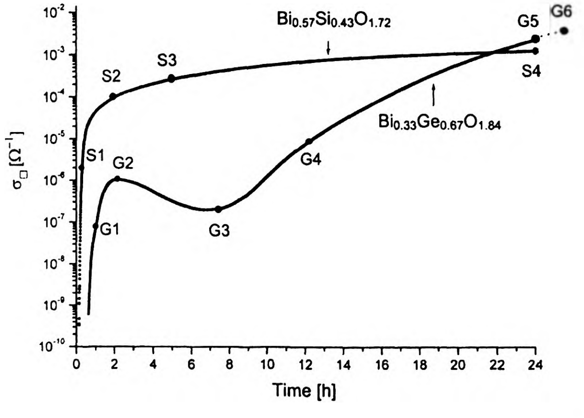

Fig. 1. Time dependence of surface conductivity of $Bi_{0.33}Ge_{0.67}O_{1.84}$ and $Bi_{0.57}Si_{0.43}O_{1.72}$ glasses during heat treatment at 613 K.

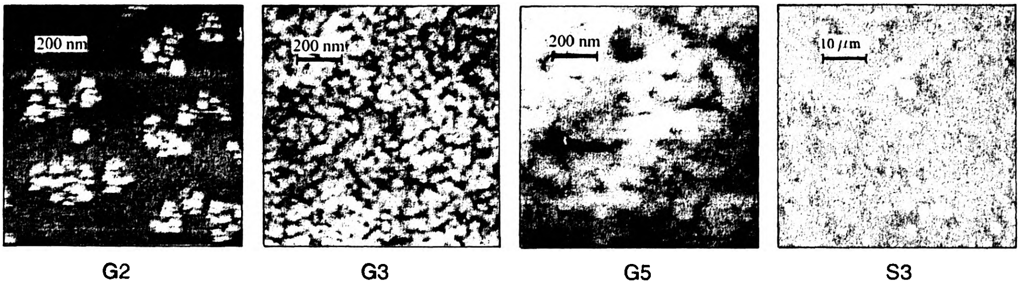

Fig. 2. AFM pictures of $Bi_{0.33}Ge_{0.67}O_{1.84}$ (G2, G3 and G5) and $Bi_{0.57}Si_{0.43}O_{1.72}$ (S3) glass samples.

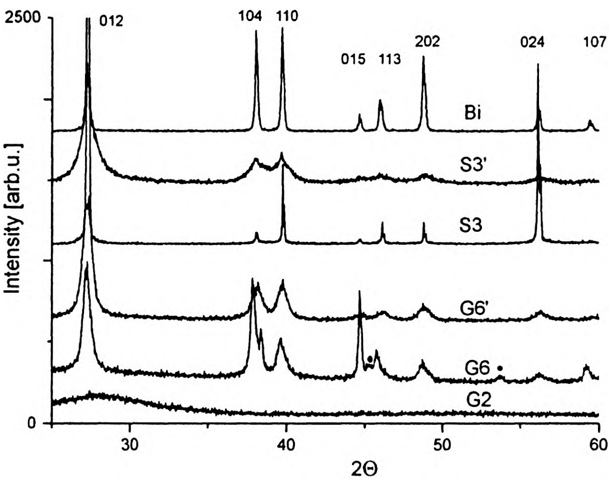

Fig. 3. X-ray diffraction spectra of rhombohedral bismuth, G2, G6, G6', S3 and S3' samples. The samples G6' and S3' are G6 and S3 after removing the outer Bi layer. Asterisk marks Ge peaks. The plots are shifted for better view.

Contrary to bismuth germanate glass, the conductivity of $Bi_{0.57}Si_{0.43}O_{1.72}$ sample continuously increases during reduction. The capital letters marked in the figure denote reduction times which were applied to particular samples subjected to further studies.

The AFM pictures of G2, G3, G5 and S3 samples are presented in Fig. 2. The flat surface of glass with a few bismuth droplets (G2), a layer of connected or disconnected droplets (G3), multi-layer granular systems (G5) and large bismuth spheres (S3) are visible in the figure.

The results of X-ray diffraction measurements of studied samples and rhombohedral bismuth [7] are shown in Fig. 3. The spectra of as-quenched glass and the samples reduced for a short time (G1 and G2) show a halo pattern with no peaks (only sample G2 is shown in Fig. 3). Glasses annealed in hydrogen for 24 h and 44 h exhibit a series of peaks characteristic of rhombohedral crystalline Bi (only sample G6 is shown in Fig. 3). They also show some peaks which correspond to germanium. The spectra denoted as G6' and S3' correspond to G6 and S3 samples after removing the very top layer from their surface. This layer was removed by careful cleaning of the surface.

4. Discussion

Properties of the bismuth germanate and bismuth silicate glasses heated in hydrogen atmosphere depend both on time and temperature of reduction. We assume that during the reduction three main phenomena occur in the material: reducing of Bi^{+3} ions into neutral atoms, their agglomeration into bigger clusters and migration towards the surface of the sample. Taking it into account, we propose a simple model of the glass subjected to the reduction process. The model is illustrated in Fig. 4. In the course of reduction, forming of two conductive layers can be distinguished. One is the layer which contains Bi particles embedded in a GeO_2 or SiO_2 glass matrix. It is in fact a glass in which nanostructured metallic bismuth phase is contained. It means that the glass structure (continuous tetrahedra network) is not destroyed by reduction [8]. The second conducting layer is the very top one containing either the majority of Bi and small amounts of Ge in bismuth germanate glasses or only Bi in bismuth silicate glasses. Within this model we can explain the behaviour of glasses under reduction. As long as the distance between Bi nanostructures is too large for an electron tunnelling to take place, the conductivity is determined by ionic mobility. While the reduction is

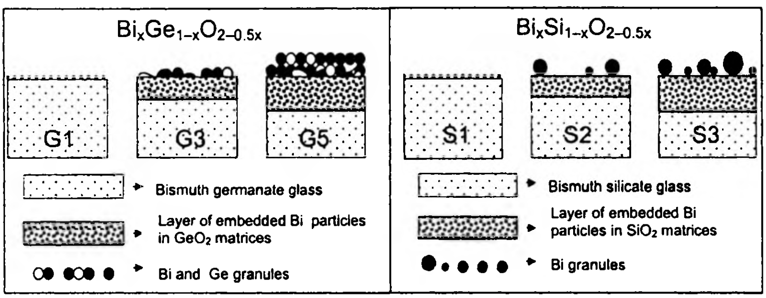

Fig. 4. Model of the layered structure of bismuth germanate and bismuth silicate glasses, reduced in hydrogen.

carried on, the concentration and dimensions of Bi clusters grow. Eventually the Bi concentration on a surface layer of glasses is sufficient for electron tunnelling through the potential barrier between metallic granules to appear. Since then, the conductivity rapidly increases (Fig. 1 – the abrupt increase in the conductivity up to points around G1 and S1). In other words, the 2D layer of Bi granules embedded in GeO_2 or SiO_2 matrices is created. Further reduction causes growing of layer thickness and threfore further increase in conductivity. In the next stage of reduction process, both the migration of bismuth atoms towards the surface and their agglomeration into large grains become significant. In the case of bismuth-silicate glasses a layer of not-bonded, spherical bismuth granules on the surface is created, whereas in bismuth germanate glasses a layer of granules strongly bonded to the surface grows. The difference between both studied materials is that Ge^{+3} ions are also reduced into neutral atoms while Si^{+3} ions are not. It causes that only in bismuth germanate glasses a decrease in conductivity occurs (from G2 to G3 in Fig. 1). If the reduction proceeds, at a certain time the concentration of Bi granules in the surface layer attains a percolation threshold (near the point G3 in Fig. 1) and the increase in conductivity is observed. It means that the continuous layer of Bi granules is created and its electrical properties begin to determine surface conductivity of the reduced samples. Further reduction causes an increase in the thickness of the outer layer.

Our model of reduced glasses also agrees very well with the results of XRD analysis, in which both layers can be observed (Fig. 3). The very top surface layer can be seen in the XRD spectra of specimens G6 and S3, while the inner one – in the samples G6' and S3' (which are the same G6 and S3 samples after removing the outer layer). It is clearly seen that the XRD reflexes corresponding to the Bi granules in the outer layer are considerably narrower than those corresponding to bismuth nanoparticles embedded in GeO_2 and SiO_2 matrices. The analysis of XRD peaks broadening shows that the diameter of embedded Bi nanoparticles in reduced G6' and S3' samples is about 10 nm and 5 nm, respectively. The thickness of an inner layer of G5 sample is about 2 μm, whereas S4 sample is 23 μm. These results show that bismuth silicate glasses are reduced more rapidly than bismuth germanate glasses.

Further support of the above model comes from AFM results (Fig. 2) where the outer layer of Bi and Ge granules is visible. The diameter and height of droplets on the surface of G2 sample are about 30 nm and 10 nm, respectively. Diameters of granules on the surface of G3 and G5 are about 30–35 nm, while on S3 sample up to about 10 μm.

5. Conclusions

An interesting property of bismuth germanate glasses is that in the course of reduction in hydrogen atmosphere they develop two conducting layers an their surface. One of them is a layer of Bi nanoclusters embedded in germanate glass matrix. The second is a layer of mixture of Bi and Ge granules on the surface.

A simple two-layer model of reduced glasses, based on XRD and AFM studies, explains the evolution of electrical properties of the materials during the reduction process.

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