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The properties of reduced Bi-Ge-O glasses for thermoelectric devices

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Abstract

The bismuth-germanate glasses have been investigated to examine their applicability for thermoelectric devices. In order to increase their electrical conductivity, the $25Bi_2O_3$–$75GeO_2$ glass samples have been reduced at 340-380°C for 10 hours in hydrogen. It has been shown that such heat treatment in H_2 leads to the reduction of metal ions Bi^{3+} and Ge^{4+} into neutral atoms and the formation of metal grains both in an amorphous glass matrix and on the glass surface. The bulk electrical conductivity of the reduced $25Bi_2O_3$–$75GeO_2$ sample measured at 100°C is ~ 2.6 Scm^{-1}, whereas the Seebeck coefficient of this glass estimated in a temperature range 20-100°C in reference to Pt is α=(-57.5±0.5) μVK^{-1}.

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Keywords: bismuth-germanate glass; reduction; electrical conductivity; Seebeck coefficient; power factor

1. Introduction

Bismuth-germanate glasses have wide application in the field of glass ceramics, layers for optical and optoelectronic devices, thermal and mechanical sensors, infrared transmitting windows and as active media for Raman optical fibre amplifiers [1]. Their interesting properties result from the coordination changes in bismuth and germanium. Germanium oxide is a typical glass former while bismuth oxide is a conditional glass former [2]. If the bismuth-germanate glass is annealed in hydrogen atmosphere, it causes the reduction of metal ions Bi^{3+} and Ge^{4+} into neutral atoms and the formation of metal grains both in an amorphous glass matrix and on the glass surface. If a

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certain critical grain concentration is achieved, the electron tunneling between the grains becomes possible. Further reduction leads to the connecting of metal grains and to the formation of continuous, metallic layer on the surface of the glass. Thus an increase in the surface electrical conductivity, even of several orders of magnitude, is observed [3]. In this way the oxide glasses can be modified to obtain a kind of 'phonon-glass electron-crystal' [4] and make them interesting materials for application in thermoelectric devices. These devices are particularly interesting due to the continuously increasing world's demand for energy. One of the ways of energy saving is to scavenge the waste heat with thermoelectric generators. In simple words every thermoelectric device consists of couples of n- and p-type conducting materials which are wired electrically in series and thermally in parallel. When an electric current is applied to the junction, the free carriers move away from the junction and cool it, what is known as Peltier effect. If a temperature gradient is applied, the mobile charge carriers at the hot end tend to diffuse to the cold end, producing an electrostatic potential (V). This is known as the Seebeck effect.

In order to estimate the thermoelectric material usability for both heat generation and cooling as well as for power generation some parameters should be determined: Seebeck coefficient (α), electrical conductivity (σ) and thermal conductivity (κ). Thus the dimensionless figure of merit can be defined: $ZT=\alpha^2T\sigma/\kappa$ [5]. According to this formula, the higher is the Seebeck coefficient and electrical conductivity of material and the lower is thermal conductivity, the better is the material from the thermoelectric applications point of view. Thus oxide glasses, which exhibit some of the lowest lattice thermal conductivities are interesting candidates for thermoelectric applications. However, the procedure of effective increase of their electrical conductivity should be elaborated.

In this work the bismuth-germanate glasses after heat treatment at 340-380°C in hydrogen have been investigated. After the process of reduction in hydrogen the metal ions are reduced to neutral atoms which form metal grains both in an amorphous glass matrix and on the glass surface. The aim of this paper is to present and discuss the structure, electrical conductivity and Seebeck coefficient of the surface layer forming on the $25Bi_2O_3$–$75GeO_2$ after the reduction in hydrogen at temperature 340°C.

2. Experimental

The $25Bi_2O_3$–$75GeO_2$ glass has been produced from appropriate reagent grade oxides and nitrides. First, the reagents were pulverised in an agate mortar and then melted in a platinum crucible at 1150°C in air. Pouring them on a stainless steel plate quenched the melts. Then obtained samples were annealed at 400°C in air. The glass composition has been determined by the Energy Dispersive X-ray Analysis (EDX) method. According to the fact that bismuth could have evaporated during the fabrication process, the final composition of $25Bi_2O_3$–$75GeO_2$ was $Bi_{0.39}Ge_{0.61}O_x$. In the next step the polished glass pellets were reduced at 340-380°C in H_2 for 10 hours. During the reduction process the changes of glasses resistivity were registered by the conventional 2-wire method equipment. The surface electrical conductivity of the finally reduced glasses was also measured by the 2-wire technique and calculated from the equation: $\sigma_{\square}=dR^{-1}l^{-1}$, where R is the resistivity of sample, d is the distance between the electrodes and l is the length of electrodes.

The X-Ray Diffraction (XRD) method was used to determine the material composition and to confirm the glassy state of the reduced samples. The Scanning Electron Microscopy (SEM) and the Atomic Force Microscopy (AFM) techniques enabled the analysis of samples morphology. The Seebeck coefficient of reduced glasses was measured with the use of homemade equipment in the temperature range 20-100°C in reference to Pt.

3. Results and discussion

The results of X-Ray Diffraction analysis obtained for $25Bi_2O_3$–$75GeO_2$ glass before and after reduction at 340°C for 10h in hydrogen are shown in Fig.1. The halo pattern with no peaks presented in Fig.1a confirms the glassy state of $25Bi_2O_3$–$75GeO_2$ sample before reduction. This glass is dark brown and its density is $\rho=6.70$ gcm^{-3}. After heat treatment in hydrogen the sample covers with a glossy, black layer. The XRD spectrum of the reduced $25Bi_2O_3$–$75GeO_2$ sample is presented in Fig.1b. Most of diffraction peaks visible in this pattern can be attributed to crystalline bismuth, but also some peaks which correspond to crystalline germanium are visible in this XRD pattern.

The SEM images of the surface and the cross section of the $25Bi_2O_3$–$75GeO_2$ samples reduced at 340°C for 10h are presented in Fig.2. It is evident that after heat treatment in hydrogen many nanometer size grains are formed on

the surface of this glass (Fig.2a). According to the XRD investigations they can be identified as nanograins of crystalline bismuth and germanium. As it is shown in Fig.2b, these grains form a continuous, 5 μm-thick layer. However, it has been reported in the literature [6] that a presence of two conductive layers on the surface of reduced sample is also possible. One is the layer, which contains Bi particles embedded in a GeO_2 glass matrix, and the latter is the very top layer containing either connected or not grains of Bi and a small amount of Ge.

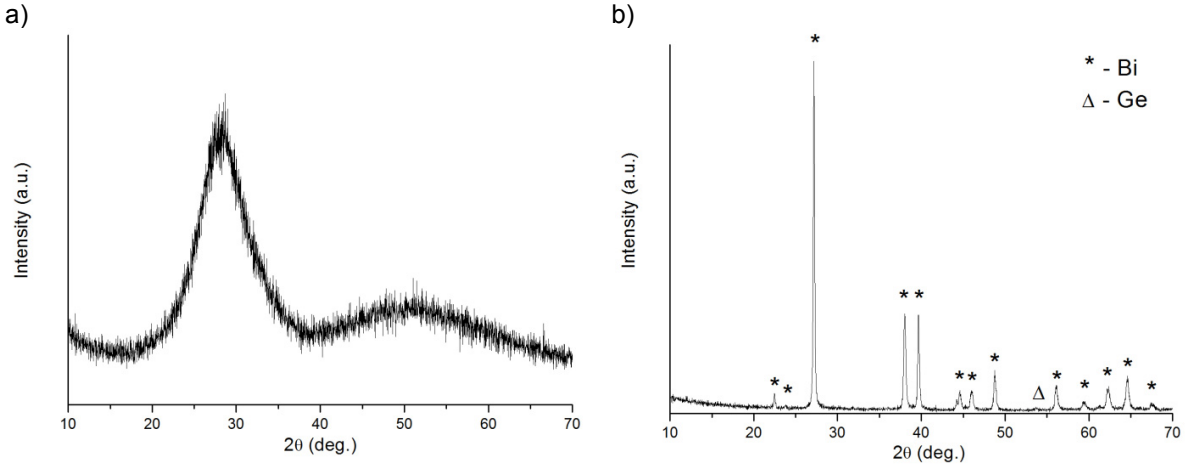

Fig.1: X-Ray Diffraction plots of (a) $25Bi_2O_3$–$75GeO_2$ glass and (b) layer on the glass surface after reduction in hydrogen.

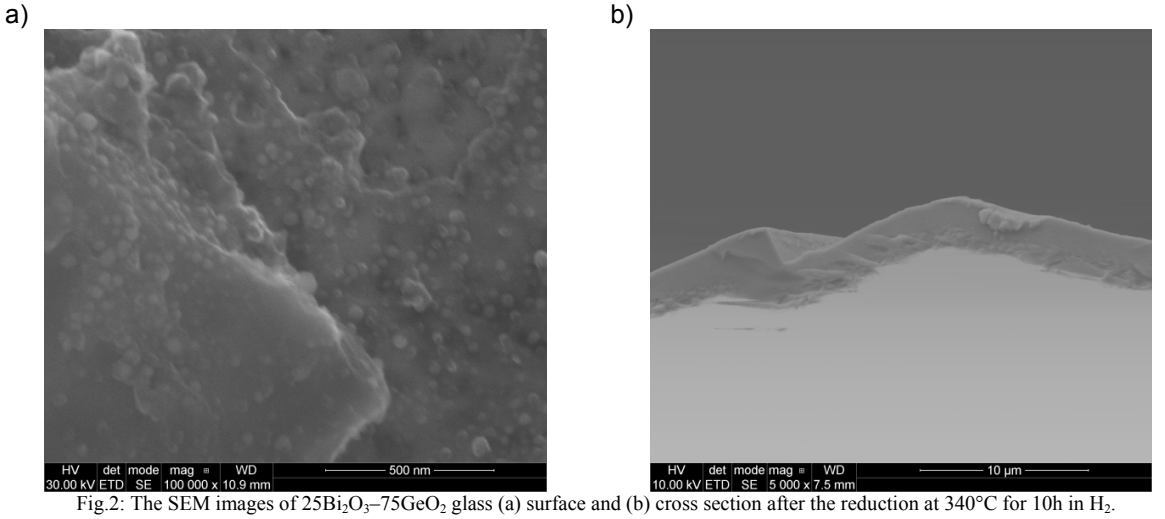

Fig.2: The SEM images of $25Bi_2O_3$–$75GeO_2$ glass (a) surface and (b) cross section after the reduction at 340°C for 10h in H_2.

The plot presenting the time dependence of surface conductivity of $25Bi_2O_3$–$75GeO_2$ glass during heat treatment at 340°C for 10h in hydrogen is shown in Fig.3. It can be divided into four areas. First one is below t_p=2500s, when the total electrical surface conductivity is below the measuring range of the applied equipment. As a consequence of reduction process the atoms of neutral bismuth occur and agglomerate into clusters. As long as they remain separated, the surface electrical conductivity is determined by ionic mobility and does not change with reduction time. The second area begins at t_p, where the total surface conductivity increases rapidly and reaches the maximum value at 7500s. At this time of reduction the concentration of Bi nanoclusters is high enough to allow tunnelling of electrons trough the potential barrier between metallic granules. However, after reaching a maximum value, the surface conductivity starts to decrease slowly during further reduction (third area). According to literature reports [6] it may be explained by the changes of surface morphology. These changes result from both the migration of bismuth atoms to the glass surface as well as from the reduction of GeO_2 matrix. The nanoclusters of bismuth tend to connect

in order to form larger agglomerates. For a short time of lasting reduction these agglomerates can remain separated, what will result in a decrease of surface electrical conductivity. After reaching a minimum value at 14500 s the surface conductivity of the reduced $25Bi_2O_3$–$75GeO_2$ glass increases rapidly (fourth area begins). This increment may result from the fact that the Bi grains have reached the percolation threshold and thus the electron conductivity begins to be the dominant mechanism of charge carrier transport. Further reduction causes the increase of thickness of the conducting layer.

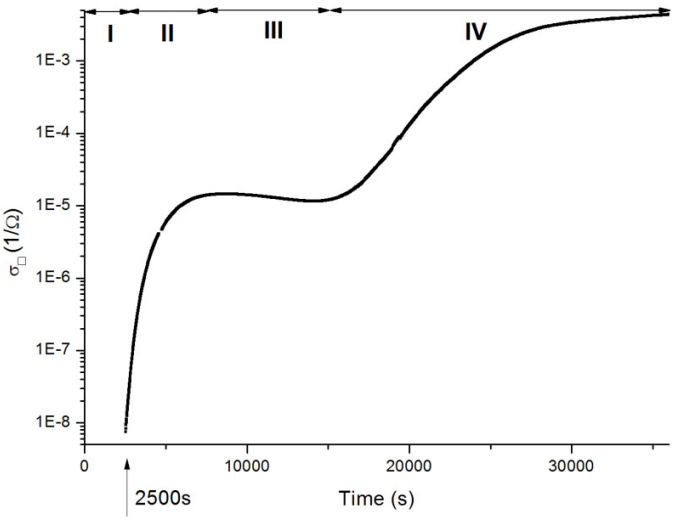

Fig.3: The time dependence of surface conductivity of $25Bi_2O_3$–$75GeO_2$ glass during heat treatment in hydrogen at 340°C for 10h.

The surface conductivity plot of reduced $25Bi_2O_3$–$75GeO_2$ glass as a function of temperature during the sample cooling is presented in Fig.4. In the first step this sample has been cooled from 345°C to the room temperature. A significant drop of surface electrical conductivity was noticed at 228°C. This change in the $\sigma_{\square}(T)$ slope can be explained by a solidification of overcooled bismuth. Then the sample was heated up to 345°C once again. During this process the electrical conductivity increased almost 3 times at temperature close to the melting point of bismuth (271°C). In the next step, during following cooling of the sample, its surface electrical conductivity dropped once again at 226°C due to the solidification of overcooled bismuth. These observations are in agreement with the literature reports [6,7].

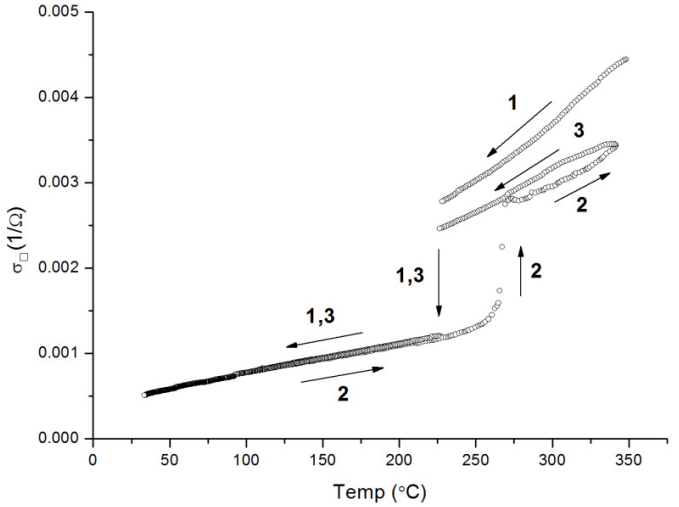

Fig.4: The surface conductivity plot of reduced $25Bi_2O_3$–$75GeO_2$ glass as a function of temperature (1-cooling, 2-heating, 3-cooling).

As the average thickness of the conducting, metallic layer has been estimated as 3 μm, the bulk electrical conductivity value at 100°C is ~ 2.6 Scm^{-1} It is not surprising that this value is much lower than value 7700 Scm^{-1} reported for a neutral Bi [8]. It can be explained by a structure of the layer formed on the surface of the investigated glass. It is not a defect-free, continuous, metallic layer, but it consists of many nanometre size grains. The existence of many grain boundaries can limit the process of charge carriers transport. Apart of that also the granules of neutral germanium can be found in this layer. The conductivity of Ge is over 3 orders of magnitude lower than the conductivity of Bi. Thus the layer, which is a composite of neutral bismuth and germanium nanoclusters, will have lower electrical conductivity than pure bismuth. Moreover, it is possible that bismuth oxides are formed on the very top surface of the sample. Their existence can also limit the electrical conductivity of the conducting layer.

The Seebeck coefficient of the reduced glass estimated in a temperature range 20-100°C in reference to Pt is $\alpha=(-57.5\pm0.5)\ \mu VK^{-1}$. It is lower, but of the same order of magnitude as the value reported in the literature [9]. This difference may result from the microstructure of the samples surface layer, as well as from the presence of germanium nanogranules which can depress the thermoelectric properties of the reduced glasses. The power factor known as $P=\alpha^2\sigma$ has been estimated as ~ $(8.6\pm0.2)\cdot10^{-3}\ \mu WK^{-2}cm^{-1}$ for the reduced $25Bi_2O_3–75GeO_2$ glass at 100°C.The relatively low value of the power factor results from the structure of the metallic layer, as it has been explained for the bulk electrical conductivity. However, it can be supposed that a modification of $25Bi_2O_3–75GeO_2$ glass structure, for example in a way of reduction of glass powder instead of bulk sample, can improve the thermoelectric parameters of this material. Thus the $25Bi_2O_3–75GeO_2$ can be considered as a potential candidate for thermoelectric applications.

4. Conclusions

It has been shown that both structural and electrical properties of bismuth-germanate glasses after heat treatment at 340-41-380°C in hydrogen (reduction) change significantly. It results from the fact that Bi^{3+} and Ge^{4+} ions are reduced to neutral atoms which form metal grains both in an amorphous glass matrix and on the glass surface. In the case of $25Bi_2O_3–75GeO_2$ glass reduced at 340°C even for less than 1 hour a continuous layer of bismuth nanogranules is formed and its electrical properties determine the surface conductivity of the reduced sample. However, further reduction leads to a slight drop of surface electrical conductivity what can result from both the migration of bismuth atoms to the glass surface as well as from the reduction of GeO_2 matrix. After 8.5h of reduction a stable system is formed and the glass electrical conductivity does not change any more. The bulk electrical conductivity of this sample measured at 100°C was determined as 2.6 Scm^{-1} and the Seebeck coefficient at this temperature in reference to Pt was found to be $\alpha=(-57.5\pm0.5)\ \mu VK^{-1}$. These parameters, as well as the expected low thermal conductivity, make reduced bismuth-germanate glasses interesting materials for application in thermoelectric devices.

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