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

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Abstract

The structural and electrical properties of germanium-antimonate glasses after heat treatment in hydrogen have been determined. In the case of $50GeO_2$-$50Sb_2O_3$ glass reduced at 340°C even for less than 1 hour a continuous layer of antimony granules is formed and its electrical properties determine the surface conductivity of the reduced sample. The bulk electrical conductivity at 100°C of this sample was determined as 1000 Scm^{-1} and the Seebeck coefficient at this temperature in reference to Pt was found to be $\alpha=(17.2\pm0.5)\ \mu VK^{-1}$.

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Keywords: germanium-antimonate glass; reduction; electrical conductivity; Seebeck coefficient; power factor

1. Introduction

The continuously increasing world's demand for energy drives various investigations in the field of effective energy managing. One of them is the scavenging of waste heat with thermoelectric generators. In general, every thermoelectric device consists of two types of conducting materials. One is a p-type conductor (contains holes) and second is an n-type conductor (contains electrons). They 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. These simple physical phenomena make thermoelectric devices worth of attention as they are silent, reliable, scalable and have no moving

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parts. They can be used in industrial processes, automotive exhaust as well as in home heating in order to convert the waste heat into electrical power.

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: $ZT=\alpha^2T\sigma/\kappa$ [2]. 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.

Oxide glasses exhibit some of the lowest lattice thermal conductivities. However, their electrical conductivity is also very low. In order to make glasses useful for thermoelectric devices they should be modified to obtain a kind of 'phonon-glass electron-crystal' [1].

One of the ways to increase the electrical conductivity of the oxide glass it to heat it in the hydrogen atmosphere (reduction process). This procedure causes the reduction of metal ions and the formation of metal grains both in an amorphous glass matrix and on the glass surface. If a 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 work the germanium-antimonate glasses after heat treatment at 340-410°C in hydrogen have been investigated. After the process of reduction in hydrogen the Ge^{4+} and Sb^{3+} ions are reduced to neutral atoms which may 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 $50GeO_2$-$50Sb_2O_3$ after the reduction in hydrogen at temperature 410°C.

2. Experimental

The $50GeO_2$-$50Sb_2O_3$ 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 final composition $Ge_{0.34}Sb_{0.66}O_x$ of the glass has been determined by the Energy Dispersive X-ray Analysis (EDX) method and it agrees with the initial composition of reagents. In the next step the polished glass pellets were reduced at 410°C in H_2 for 10 hours. The initial investigations indicated that the reduction of $50GeO_2$-$50Sb_2O_3$ glass takes place even at 340°C, but at 410°C this process is fast and the layer forming on the surface is structurally homogenous. During the reduction process the changes of glasses resistivity were registered by the conventional 2-wire method equipment. The surface electrical conductivity ($\sigma_\square$) of the finally reduced glasses was measured by the 4-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 method (XRD) 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 $50GeO_2$-$50Sb_2O_3$ glass before and after reduction at 410°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 $50GeO_2$-$50Sb_2O_3$ sample before reduction. This glass is light green and its density is $\rho=5.17$ gcm^{-3}. After heat treatment in hydrogen the sample covers with a glossy, black layer. The XRD spectrum of the reduced $50GeO_2$-$50Sb_2O_3$ sample is presented in Fig.1b. All the diffraction peaks visible in this pattern can be attributed to crystalline antimony. According to the literature reports [4], the presence of crystalline germanium was also expected on the glass surface after reduction, but it is not visible in the XRD pattern.

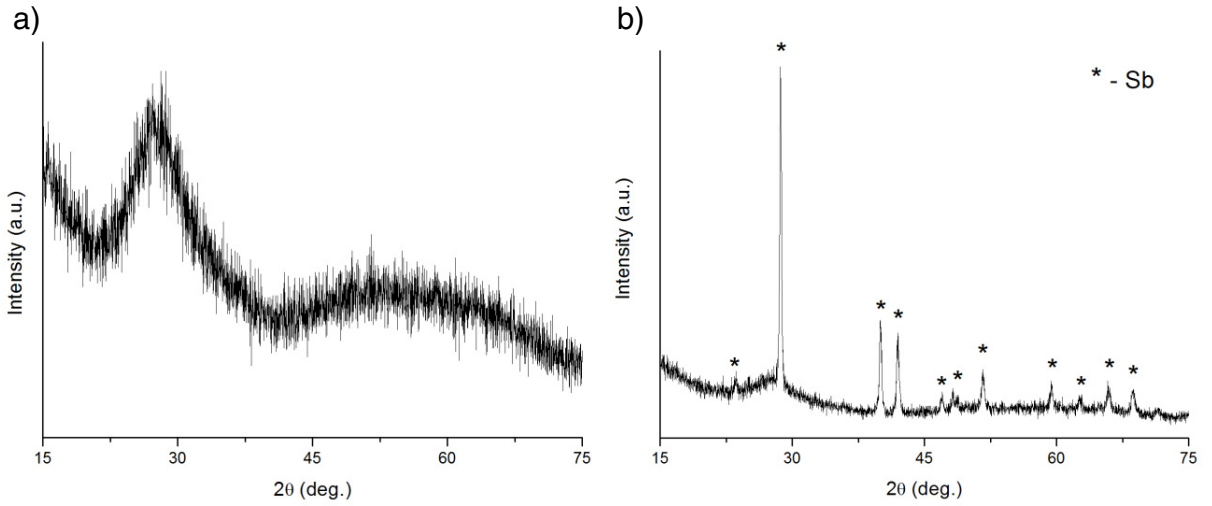

Fig.1: X-Ray Diffraction plots of (a) $50GeO_2$-$50Sb_2O_3$ glass and (b) layer on the glass surface after reduction in hydrogen.

The SEM images of the surface and the cross section of the reduced $50GeO_2$-$50Sb_2O_3$ samples are presented in Fig.2. It can be seen that after reduction at 410°C for 10h in H_2 a 500-700 nm thick layer of nanoclusters (diameter 30-100 nm) is formed on the surface of $50GeO_2$-$50Sb_2O_3$ glass. The initial investigations exhibited that this layer contains mostly of neutral Sb^0 atoms, however the presence of neutral Ge^0 atoms is also possible [5]. If they are separated, the detection of such nanograins may be below the measuring resolution of the applied equipment.

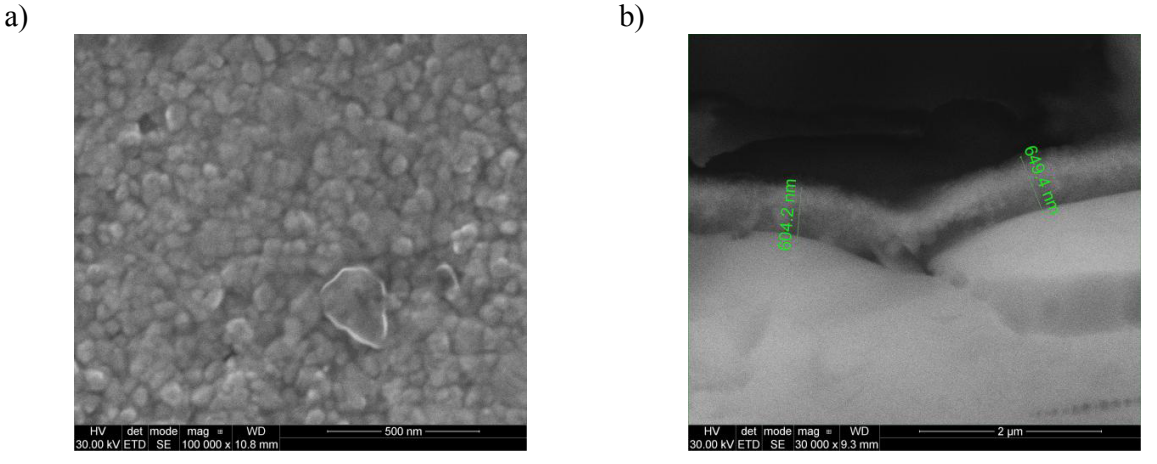

Fig.2: The SEM images of $50GeO_2$-$50Sb_2O_3$ glass (a) surface and (b) cross section after the reduction at 410°C for 10h in H_2.

The plot presenting the time dependence of surface conductivity of $50GeO_2$-$50Sb_2O_3$ glass during heat treatment at 410°C for 10h in hydrogen is shown in Fig.3. It can be divided into two areas. First one is below t_p=2500s, when the total electrical conductivity is below the measuring range of the applied equipment. The second area starts at t_p, where the total electrical conductivity increases rapidly and reaches the maximum value at 7500s. This behaviour can be explained by the migration of antimony atoms to the surface of sample, where the very top layer containing either connected or not connected grains of Sb is formed. As long as they remain separated, the surface electrical conductivity is determined by ionic mobility and does not change with reduction time (first area in Fig.3). After the time of reduction equal t_p the concentration of Sb nanoclusters attains a percolation threshold and the electrical conductivity of samples increases significantly. Then the continuous layer of antimony granules is formed and its electrical properties determine the surface conductivity of the reduced sample. At this stage a change of size and

concentration of antimony granules takes place. Thus a slight minimum at 20000s is visible in the surface conductivity plot. Further reduction causes the increase of thickness of this layer.

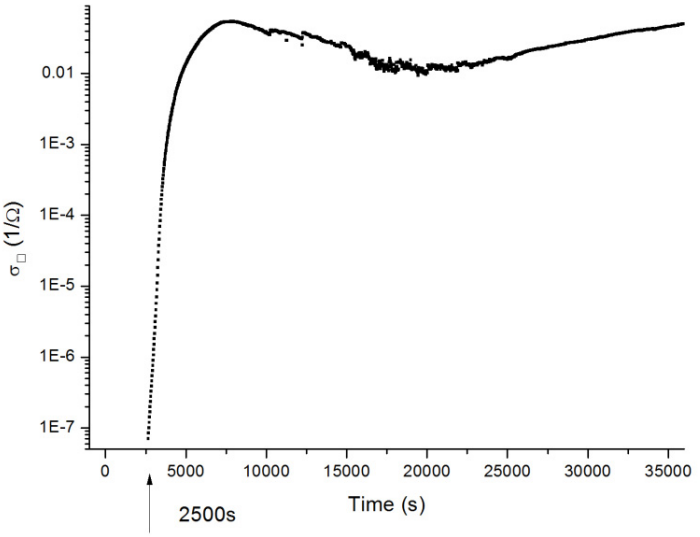

Fig.3: The time dependence of surface conductivity of $50GeO_2$-$50Sb_2O_3$ glass during heat treatment in hydrogen.

The surface conductivity plot of reduced $50GeO_2$-$50Sb_2O_3$ glass as a function of temperature is presented in Fig.4. It confirms that the surface electrical conductivity is nearly constant (changes from 0.065 to 0.050 Ω^{-1}) in the whole temperature range. As the average thickness of the conducting, metallic layer has been estimated as 0.6 μm, the bulk electrical conductivity value at 100°C is ~ 1000 Scm^{-1}. It is not surprising that this value is much lower than the value 25000 Scm^{-1} reported for a neutral Sb [5]. 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. Moreover, it is possible that antimony oxides are formed on the very top surface of the sample. Their existence can also limit the electrical conductivity of the conducting layer.

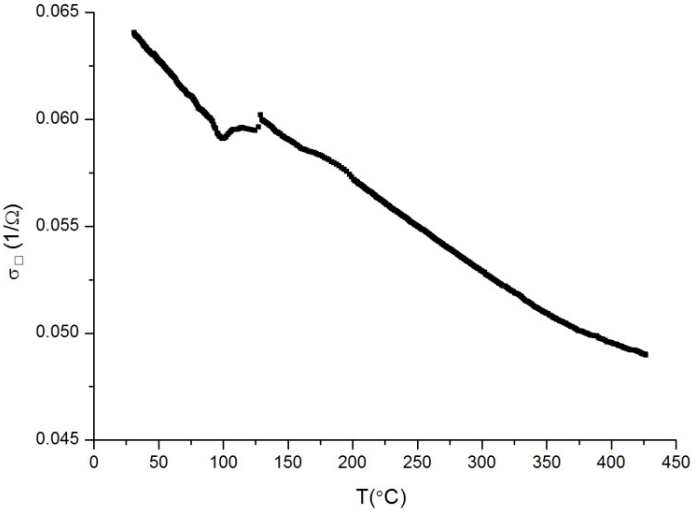

Fig.4: The surface conductivity plot of reduced $50GeO_2$-$50Sb_2O_3$ glass as a function of temperature.

The Seebeck coefficient of the reduced glass estimated in a temperature range 20-100°C in reference to Pt is $\alpha=(17.2\pm0.5)$ μVK^{-1}. It is three times lower than the value reported in the literature [6]. Thus the power factor known as $P=\alpha^2\sigma$ has been estimated as ~ (0.30 ± 0.02) $\mu WK^{-2}cm^{-1}$ for the reduced $50GeO_2$-$50Sb_2O_3$ 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 $50GeO_2$-$50Sb_2O_3$ 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 $50GeO_2$-$50Sb_2O_3$ can be considered as a potential candidate for thermoelectric applications.

4. Conclusions

It has been shown that both structural and electrical properties of germanium-antimonate glasses after heat treatment at 340-410°C in hydrogen (reduction) change significantly. It results from the fact that Sb^{3+} 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 $50GeO_2$-$50Sb_2O_3$ glass reduced at 340°C even for less than 1 hour a continuous layer of antimony granules is formed and its electrical properties determine the surface conductivity of the reduced sample. The bulk electrical conductivity measured at 100°C of this sample was determined as 1000 Scm^{-1} and the Seebeck coefficient at this temperature in reference to Pt was found to be $\alpha=(17.2\pm0.5)$ μVK^{-1}. These parameters, as well as the expected low thermal conductivity, make reduced germanium-antimonate glasses interesting materials for application in thermoelectric devices.

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