Effect of heat treatment on the galvanomagnetic properties of bulk nanostructured samples of Bi$_{85}$Sb$_{15}$ solid solution

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Abstract: Extruded bulk nanostructured samples of Bi$_{85}$Sb$_{15}$ solid solution from particles with average sizes $\sim$2-10$^5$: 950; 650; 380; 30 and 15 nm were obtained and investigated their galvanomagnetic properties in the range of $\sim$77-300 K. Were investigated samples that have not passed heat treatment, and the same samples that have passed heat treatment. It was found that the electrical and thermal properties of Bi$_{85}$Sb$_{15}$ solid solution samples significantly depend on the size of nanoparticles and post-extrusion heat treatment. Heat treatment leads to a decrease in the concentration of current carriers and to an increase in the mobility of current carriers and the total thermal conductivity of the samples under study, which is mainly due to the electronic component of thermal conductivity. The change in thermal parameters is satisfactorily explained by changes in occurring in the structure of samples during extrusion and heat treatment and correlates well with changes in the electrical parameters of these processes.

1. Introduction

Solid solutions of Bi-Sb systems, especially high-strength extruded materials based on these systems, are the most effective materials for creating various low-temperature thermo- and magneto-thermoelectric energy converters [1-6]. The extrusion method has high productivity and opens up wide opportunities for profiling thermoelement legs [7-9]. However, there are almost no studies on the regularities of the effect of grain sizes (especially in the region of nanoscale) on the transport parameters of these materials. With a decrease in the grain size, boundary effects begin to manifest themselves in the transport properties, including the processes of scattering of phonons and electrons at grain boundaries [10-11]. Nanostructuring of thermoelectrics makes it possible to use a new controllable parameter - the size of nanostructured elements - as an additional factor affecting the figure of merit, which can lead to an increase in the thermoelectric figure of merit in bulk nanocrystalline thermoelectric materials [12].

It was found that post-extrusion annealing leads to a decrease in the dislocation density and defect concentration in the samples of Bi-Sb systems [13]. Therefore, the study of the galvanomagnetic properties in nanostructured extruded samples with different grain sizes that have passed and did not
undergo annealing in a wide range of temperatures and magnetic field strengths is of certain scientific and practical interest.

Taking into account the above, in order to study the influence of annealing and nanoscale effects on the electrical and thermal properties of bulk nanostructured samples of solid solution Bi$_{85}$Sb$_{15}$, bulk nanostructured extruded samples, Bi$_{85}$Sb$_{15}$ materials were obtained in this work and their transport properties were investigated in the range of $\sim$77$\div$300 K.

2. Experimental technique

The synthesis of the Bi$_{85}$Sb$_{15}$ composition was carried out by direct fusion of the components in the corresponding stoichiometry in a quartz ampoule evacuated to a residual pressure of $\sim$10$^{-2}$ Pa. "Vi-000" brand Bismuth and "Su-0000" brand antimony were used as the initial components.

Nanosized particles of Bi$_{85}$Sb$_{15}$ were obtained using an AGO-2 ball mill. The size of particles in the powder was changed by changing the time of crushing the starting material in the mill. The average size of particles in the powder were determined on an XRD D8 ADVANCE X-ray unit, Bruker, Germany based on diffraction spectra using the Sherrer formula [14] and using the TOPAS-4.2 and EVA software, the size of crystallites were specified, equal to $\sim$2$\times$10$^3$; 950; 650; 380; 30 and 15 nm.

The powders of the Bi$_{85}$Sb$_{15}$ solid solution were pressed at room temperature and a pressure of $\sim$3.5 T/cm$^2$, briquettes $\sim$30 mm in diameter, convenient for extrusion. Extrusion was carried out on an MS-1000 hydraulic press from a diameter of $\sim$30 mm to a diameter of 6 mm using special equipment. The technological parameters of the extrusion process (temperature, pressure, drawing speed, etc.) were chosen so that the formation of extruded rods took place under superplastic conditions without macro- and micro-damage.

Samples were cut from various extruded rods on an A207.40M electric spark installation in the form of rectangular parallelepipeds with dimensions of 3$\times$5$\times$12 mm. The damaged layer formed on the surface of the samples during cutting was removed by electrochemical etching in a KOH + C$_6$H$_{12}$O$_6$ + H$_2$O solution. The samples were annealed in evacuated to a pressure of $\sim$10$^{-3}$ Pa in quartz ampoules at a temperature of $\sim$503 K for 2 hours.

The electrical conductivity ($\sigma$), the coefficients of thermo-emf ($\alpha$), Hall ($R_H$) and thermal conductivity ($\chi$) of samples that have not undergone annealing and the same samples that have undergone annealing after extrusion in the range of $\sim$77$\div$300 K and magnetic field strength ($H$) up to $\sim$74 $\times$ 10$^4$ A/m were investigated. The electrical and thermal parameters were measured by the method described in [15] along the length of the sample; in the direction of extrusion. In the measurements, we used a cryostat with a design that allows one to measure $\sigma$, $\alpha$, $R_H$ and $\chi$ in one mounting of the sample. Electrical conductivity and Hall coefficient were measured on a direct current method. The probes were preliminarily soldered onto the sample to remove the voltage drop arising during measurements of $\sigma$, $R_H$ and thermo-emf when measuring the coefficient $\alpha$. The temperature gradient created along the sample during the measurements of $\alpha$ and $\chi$ was determined using two copper – constantan thermocouples, one of whose heads were soldered onto the sample.

To eliminate the electrical asymmetry of the probes, measurements of the voltage drop across the probes in determining were carried out in two opposite directions of the current through the sample. To eliminate the influence of asymmetry of Hall contacts and other parasitic emf caused by galvanomagnetic and thermomagnetic effects, $R_H$ measurements were carried out at two opposite directions of current and magnetic field. In this case, by rotating the cryostat in a magnetic field, the maximum value of the Hall voltage across the sample was achieved. Electrical conductivity and galvanomagnetic effects were measured under isothermal conditions, and thermoelectric power under adiabatic conditions. The fulfillment of these conditions was monitored by measuring the thermo-emf of the sample and directly by thermocouples soldered to the sample.

Thermal conductivity measurements were carried out by the absolute stationary method along the sample. Due to the fact that solid solutions based on bismuth-antimony have low thermal conductivity, heat loss due to radiation from the heating furnace and crystal, as well as heat carried away by the wires of the heating furnace and wires for picking up various signals are significant.
The measurements took into account the heat carried away with the above wires, as well as the heat carried away by radiation from the surface of the sample and the electric heater.

In the course of measurements, a vacuum of $\sim 10^{-3}$ Pa was created and maintained inside the cryostat where the sample was located.

Voltage values, emf and the current strength during measurements was determined using a digital voltmeter and ammeter of the B7-21 and SM3D brands.

The geometrical dimensions of the samples and the distance between the probes were determined by an MBS-1 microscope with an accuracy class of 0.005 mm.

An electromagnet was used to provide a magnetic field for measuring intensities up to 1.0 T. The error in measuring electrical parameters and thermal conductivity was $\approx 3.5\%$.

3. Results and discussion

The obtained measurement results are presented in Figures 1, 2 and in Table 1. Figure 1 shows that in the samples that have passed and did not pass heat treatment, the dependences of the coefficients $\sigma$ and $\alpha$ on the grain size at $\sim 77$ K are non-monotonic. Heat treatment leads to an increase in $\sigma$ and to a decrease in $\alpha$ in all studied samples, except for a sample with a grain size of $\sim 2 \times 10^3$ nm. With heat treatment for all samples, the coefficient of total thermal conductivity ($\chi$) increases, except for the sample with nanoparticles of 15 nm. The electronic ($\chi_e$) and lattice ($\chi_l$) components of thermal conductivity were calculated from the expressions $\chi = \chi_e + \chi_l$ and $\chi = L\alpha T$. Here $L = A/(k/e)^2$ is the Lorentz number, $k$ is the Boltzmann constant, and $e$ is the electron charge. The value of $\chi$ was estimated from the dependence of $A$ on the thermo-emf coefficient $\alpha$ [16].

### Table 1. Concentration ($n$), mobility ($\mu$) of current carriers and phonon part of thermal conductivity ($\chi_p$) of nanostructured extruded samples of Bi$_{33}$Sb$_{15}$ solid solution with different grain sizes

| Particle size in powder, nm | At $\sim 77$ K temperature | Non-annealed samples | Annealed samples |
|----------------------------|----------------------------|----------------------|------------------|
|                            | $\chi_p$, W/mK             | $\mu$, cm$^2$/V$\cdot$s | $n$, cm$^{-3}$   |
| 2 $\times 10^3$            | 2.98                       | 31833                | 0.7$\times 10^{18}$ |
| 950                        | 3.28                       | 6080                 | 5.2$\times 10^{18}$ |
| 650                        | 3.09                       | 3026                 | 15.6$\times 10^{18}$ |
| 400                        | 1.93                       | 5485                 | 12.5$\times 10^{18}$ |
| 32                         | 2.02                       | 4340                 | 15.6$\times 10^{18}$ |
| 15                         | 2.78                       | 1800                 | 31.3$\times 10^{18}$ |

At low temperatures, with a decrease in the grain size in the extruded samples, an increase in $\chi$ and a decrease in the phonon part of the thermal conductivity ($\chi_p$) are observed, as well as an increase in $\sigma$ and a decrease in $\alpha$ and $R_H$ are observed. This is due to a decrease in the size of crystals, an increase in the concentration of boundaries, which leads to an increase in the concentration of electrons and a decrease in the scattering of phonons and electrons in the samples. With an increase in the grain size, the disorientation of grains is weakened due to thermal energy during hot extrusion ($\sim 470$ K). Therefore, with an increase in the grain size, the degree of texture of the samples increases. At the same time, the perfection of the grains also grows, which leads to an increase in the mobility of current carriers $\mu$ and a certain decrease in their concentration $n$. According to the values of $R_H$ and $\sigma$ at $\sim 77$ K the Hall mobility $\mu = R_H \sigma$ of current carriers was calculated. It has been found that with an increase in the size of nanoparticles and during heat treatment, the value of $m$ in the $\mu - T^{n}$ dependence increases from 1.42$\pm$1.57 for samples without heat treatment, to 1.81$\pm$2.60 for the same samples that have undergone heat treatment. The growth of $R_H$ and $\mu$ at $\sim 77$ K after heat treatment is apparently associated mainly with a change in the concentration of defects and the parameter $A$, which
Figure 1. Temperature dependences of the coefficients of electrical conductivity ($\sigma$), thermo-emf ($\alpha$), Hall ($R_H$) and thermal conductivity ($\chi$) of extruded samples of Bi$_{85}$Sb$_{15}$ solid solution with different grain sizes that have not undergone heat treatment (a, c, e, g) and heat treated (b, d, f, h). Curves 1-6 refer to samples with grain sizes $2 \times 10^5$; 950; 650; 380; 30 and 15 nm, respectively.
Figure 2. Dependences of electrical conductivity ($\sigma$), thermo-e.m.f. ($\alpha$), Hall ($R_H$) and thermal conductivity ($\chi$) coefficients of the extruded samples of Bi$_{85}$Sb$_{15}$ solid solution with various sizes of particles before (a, c, e, g) and after (b, d, f, h) heat treatment on magnetic fields intensity at ~77 K. Curves 1-6 refer to samples with grain sizes $2 \times 10^5$; 950; 650; 380; 30 and 15 nm, respectively.
characterizes the scattering mechanism in the expression $R_0 = A/e\hbar n$, except for a sample with grain sizes $\sim 2\times10^5$ nm, where $e$ is the electron charge.

During the extrusion of nanostructured samples of the Bi$_{85}$Sb$_{15}$ solid solution, due to plastic deformation, most of the polycrystal grains are oriented so that their trigonal axis becomes parallel to the extrusion axis, i.e., a texture is formed. During plastic deformation, various defects of the crystal lattice arise simultaneously in individual grains. The degree of texture in nanostructured samples will depend on the technological parameters of the extrusion process, on the size of grains (nanoparticles) and post-extrusion heat treatment. During heat treatment, grain disorientation can also occur due to thermal energy, i.e., change in the degree of texture of the extruded sample [17]. Defects connected by boundaries between crystallites (grains) lead to the fact that samples with the minimum grain size ($\sim 15$ nm) have a high concentration of current carriers among the samples studied. The strongest change in the degree of texture upon annealing occurs in nanostructured samples with the smallest grain sizes.

With an increase in the size of particles in bulk nanostructured samples, the effect of heat treatment on the degree of texture is weakened. The experimental results show that a decrease in the size of nanoparticles leads to a decrease in mobility due to electron scattering at the boundaries of nanoparticles (Table 1). Therefore, the degree of texture during extrusion, recrystallization and disorientation of particles during heat treatment, as well as electrical and thermal parameters will depend on the size of the particles (grains) in the sample.

Figure 2 shows that with a decrease in the grain size, the magneto resistance of the samples decreases. For all samples with heat treatment, the value of the magneto resistance increases significantly. With a decrease in the grain size, the effect of heat treatment and magnetic field on the magneto resistance of nanostructured samples is weakened.

At $\sim 77$ K, the dependence of $\alpha$ on the magnetic field strength for the investigated samples with heat treatment and without heat treatment are the same and almost do not depend on $H$, except for a sample with a particle size of $\sim 2\times10^5$ nm. (Figure 2).

In a magnetic field, some redistribution of the roles of different carriers in the total current in the sample takes place. The contribution to the total current of weakly scattering current carriers decreases due to an increase in the resistance to their motion, which, at a constant total current, leads to an increase in the contribution of strongly scattered particles. In this case, the average energy of the current carriers changes. During heat treatment, scattering by acoustic phonons begins to prevail in the samples, to which fast charge carriers are more susceptible than slow ones. Therefore, in a magnetic field, the total current of fast carriers increases and, consequently, the average energy of current carriers increases. Therefore, the dependence of $\alpha$ on the magnetic field in samples with heat treatment is stronger than in samples that have not undergone heat treatment.

In the scattering of phonons in samples at low temperatures ($\sim 77$ K), texture plays a predominant role, and electrons are mainly scattered by structural defects. With an increase in the size of grains (nanoparticles), the concentration of structural defects formed during plastic deformation decreases, which leads to a decrease in the concentration of electrons $n$, $\chi_r$, to an increase in $\mu$, and to a certain increase in $\chi_p$.

During heat treatment, partial destruction of the texture and “healing” of structural defects occurs [13], which leads to a decrease in $n$, to an increase in $\mu$, $\sigma$, and $\chi_p$.

The character of the dependence of the electrical and thermal parameters on the magnetic field strength for both unannealed and annealed samples is retained even at ~300 K. However, at ~300 K, the effect of heat treatment and magnetic field on the kinetic parameters is greatly weakened.

4. Conclusion

Thus, the dependences of the electrical and thermal parameters of bulk nanostructured extruded samples of the Bi$_{85}$Sb$_{15}$ solid solution on the grain size and heat treatment show that the dominant role in the scattering of charge carriers and phonons in the samples at $\sim 77$ K is played by the grain size, defects bound by grain boundaries, and the degree of ordering (texture) of grains during extrusion, recrystallization and disorientation of crystallites during heat treatment. Heat treatment leads to a
decrease in $n$ and to an increase in $\mu$, $\chi$, $\chi_e$ and magnetoresistance. With an increase in the grain size, due to an increase in the energy required for grain orientation, the degree of texture in the samples upon deformation decreases somewhat, which leads to a weakening of the dependence of $\chi_e$ on the grain size. The change in thermal parameters is satisfactorily explained by the changes occurring in the structure of the samples during extrusion and heat treatment and correlates well with changes occurring in the electrical parameters of these processes.

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