EFFECT OF ANNEALING ON THE THERMOELECTRIC PROPERTIES OF EXTRUDED BULK NANOSTRUCTURED SAMPLES OF THE $Bi_{0,85}Sb_{0,15}$ SOLID SOLUTION

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Extruded bulk nanostructured samples of the $Bi_{0,85}Sb_{0,15}$ solid solution were obtained from particles with an average size of ~$2\cdot10^5$; 950; 650; 380; 30 and 15 nm and their thermoelectric properties were investigated in the range of ~77-300K. The samples that had not undergone heat treatment and the same samples that had undergone heat treatment were examined. It was found that the electrical and thermal properties of the $Bi_{0,85}Sb_{0,15}$ 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, an increase in the mobility of current carriers and the overall thermal conductivity of the studied samples, which is mainly due to the electronic component of thermal conductivity.

Keywords: extrusion, annealing, solid solution, nanoparticle, texture.
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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 [1-4]. The extrusion method has high productivity and gives wide possibilities to analyze thermoelement branches [5,6]. However, there is almost no work on studying the patterns of influence of particle sizes (especially in the nanosize region) on the transport parameters of these materials. With a decrease in particle size, boundary effects begin to known themselves in the transport properties, including the processes of scattering of phonons and electrons at particle boundaries [7,8]. Nanostructuring of thermoelectrics allows the use of a new controllable parameter - the size of nanostructural elements - as an additional factor influencing the figure of merit, which can lead to an increase in the thermoelectric figure of merit in bulk nanocrystalline thermoelectric materials [9].

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 [10]. Therefore, the study of galvanomagnetic properties in extruded nanostructured samples with different particle sizes, annealed and not annealed 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 the $Bi_{0,85}Sb_{0,15}$ solid solution, in this work extruded bulk nanostructured samples, $Bi_{0,85}Sb_{0,15}$ materials, were obtained and their transport properties were studied in the range ~77÷300K.

2. EXPERIMENTAL PART

The synthesis of the $Bi_{0,85}Sb_{0,15}$ composition was carried out by direct alloying of the components in the appropriate stoichiometry in a quartz ampoule removed to a residual pressure of ~10^{-2} Pa. Bismuth of the "Vi-000" grade and antimony of the "Su-0000" grade were used as the starting components.

Nano-sized $Bi_{0,85}Sb_{0,15}$ particles were obtained using an AGO-2 ball mill. The particle size in the powder was changed by changing the time of crushing the source material in the mill. The average particle sizes in the powder were determined on an XRD D8 ADVANCE X-ray installation, Bruker, Germany based on diffraction spectra using the Scherrer formula [11] and using the TORAS-4.2 and EVA program, the crystallite sizes were specified to be ~$2\cdot10^5$; 950; 650; 380; 30 and 15 nm.

$Bi_{0,85}Sb_{0,15}$ solid solution powders were pressed at room temperature and pressure ~3.5 T/cm^2 into briquettes with a diameter of ~30 mm, which is convenient for extrusion. Extrusion was carried out on an MS-1000 hydraulic press from a diameter of 30 mm to a diameter of 6 mm using special equipment. Technological parameters of the extrusion process (temperature, pressure, drag velocity, etc.) were chosen such that the formation of extruded rods took

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place under conditions of super plasticity without macro- and micro-disturbances.

Samples for research were cut out from various extruded rods using an A207.40M electric spark installation in the form of rectangular parallelepipeds with dimensions of 3 x 5 x 12 mm. The damaged layer formed on the surface of the samples during cutting was removed by electrochemical etching in a solution of $KOH+C_4H_4O_6+H_2O$. Annealing of the samples was carried out in quartz ampoules evacuated to a pressure of ~10^{-1} Pa at a temperature of ~503 K for 2 hours.

Electrical conductivity (σ), thermo-electromotive force (α), Hall (R_H) and thermal conductivity (χ) coefficients of samples that were not annealed and the same samples that were annealed after extrusion were studied in the range ~77-300K and magnetic field strength (H) up to ~$74x10^4$ A/m. Electrical and thermal parameters were measured by the method described in [12] along the length of the sample, i.e. in the direction of extrusion. The measurements used a cryostat with a design that allows one to measure σ, α, R_H and χ in one sample installation. Electrical conductivity and Hall coefficient were measured at direct current. Probes were pre-soldered onto the sample to remove the voltage drop that occurs when measuring σ, R_H and thermo-electromotive force when measuring the coefficient α. The temperature gradient created along the sample during measurements of α and χ was determined using two copper-constantan thermocouples, one of whose heads was soldered to the sample.

To eliminate the electrical asymmetry of the probes, measurements of the voltage drop across the probes when determining σ were carried out in two opposite directions of current through the sample. To eliminate the influence of asymmetry of Hall contacts and other parasitic electromotive forces caused by galvanomagnetic and thermomagnetic effects, R_H measurements were carried out in 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 on the sample was achieved. Electrical conductivity and galvanomagnetic effects were measured under isothermal conditions and thermopower under adiabatic conditions. The execution of these conditions was controlled by measurements of the thermo- electromotive force of the sample and directly with thermocouples soldered to the sample.

Thermal conductivity measurements were carried out using an 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 receiving various signals, are significant.

The measurements took into account the heat carried away by the above wires, as well as the heat carried away by radiation from the surface of the sample and the electric heater.

During the measurements, a vacuum of ~10^{-3} Pa was created and maintained inside the cryostat, where the sample was located.

Voltage values, electromotive force and current strength during measurements were determined using a digital voltmeter and ammeter brand B7-21 and SM3D.

The geometric dimensions of the samples and the distances 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 intensity measurements up to 1.0 Tesla.

The error in measuring electrical parameters and thermal conductivity was ~3-5%.

3. RESULTS AND ITS DISCUSSION

The obtained measurement results are presented in Figures 1, 2, 3.

From Fig. 1 it can be seen that in samples that have undergone heat treatment and have not undergone heat treatment, the dependences of the coefficients σ and α on the particle size at ~77 K are non-monotonic. Heat treatment leads to an increase in σ and a decrease in α in all studied samples, except for the sample with particle sizes ~$2 \cdot 10^5$ nm.

With heat treatment, the coefficient of total thermal conductivity (χ) increases for all samples, except for the sample with 15 nm nanoparticles. Using the expressions $\chi_L= \chi-\chi_e$ and $\chi_e= L\sigma T$, the electronic (χ_e) and lattice (χ_L) components of thermal conductivity were calculated. Here $L= A(k/e)^2$ Lorentz number, k is Boltzmann's constant, e is the electron charge. The value of A was estimated from the dependence of A on the thermo-electromotive force coefficient [13].

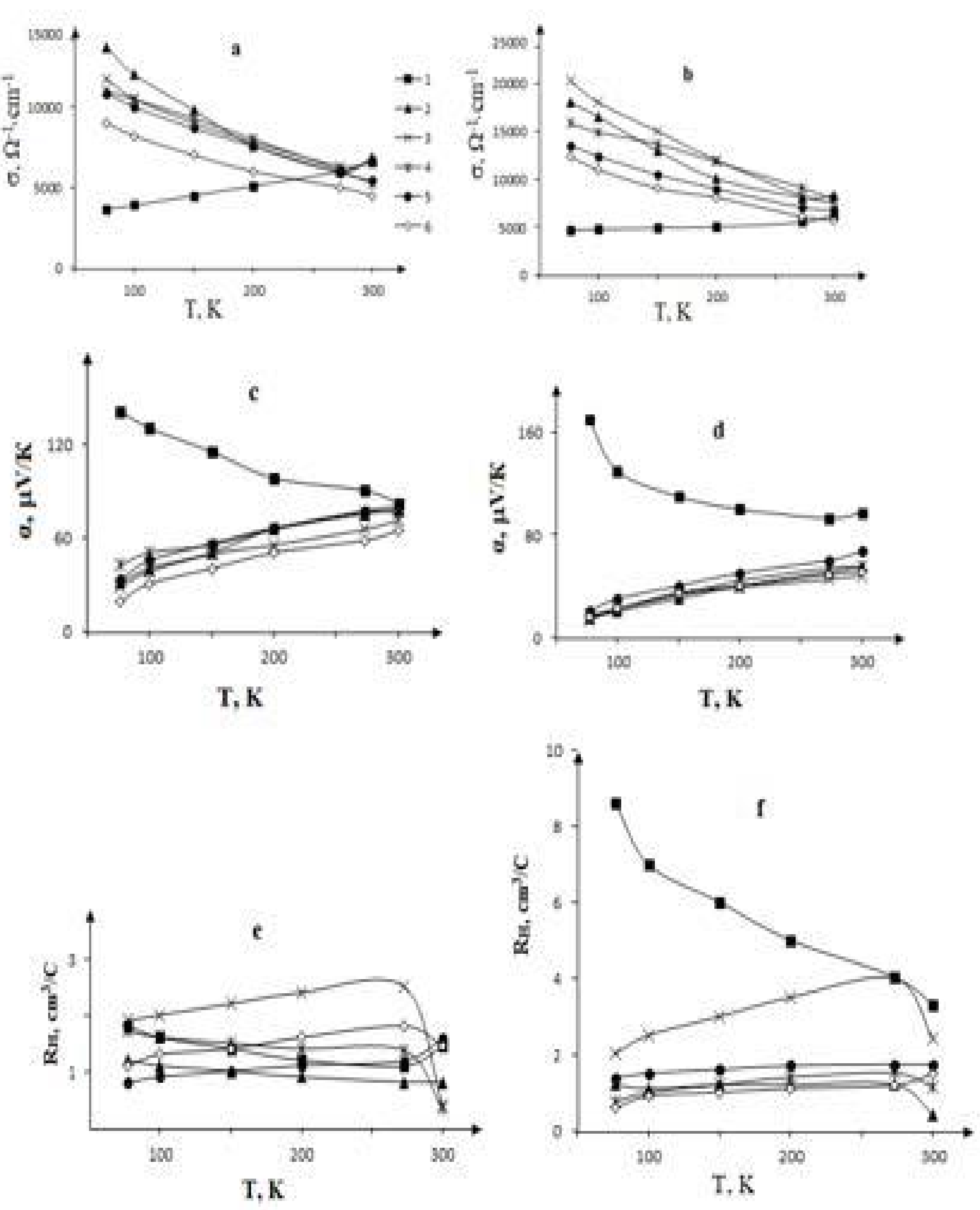
At low temperatures, with a decrease in particle size in extruded samples, an increase in χ and a decrease in the phonon part of thermal conductivity (χ_L) are observed, as well as an increase in σ and a decrease in α and R_H. This is due to a decrease in the size of the crystals and an increase in the concentration of boundaries, which leads to an increase in the electron concentration and a decrease in the scattering of phonons and electrons in the samples. As particle sizes increase, particle disorientation weakens due to thermal energy during hot extrusion (~470K). Therefore, with increasing particle sizes, the degree of texture of the samples increases. At the same time, the perfection of the particles also increases, which leads to an increase in the mobility of current carriers μ and a slight decrease in their concentration n.

From the values of R_H and σ at ~77K, the Hall mobility $\mu= R_H\,\sigma$ of current carriers was calculated. It was found that with an increase in the size of nanoparticles during heat treatment, the value of m as a function of $\mu \sim T^{m}$ increases from 1.42 ÷1.57 for samples without heat treatment, to 1,81÷2,6 for the same samples that undergone heat treatment. The increase in R_H and μ at ~77K after heat treatment is apparently associated mainly with a change in the concentration of defects and the parameter A, which characterizes the scattering mechanism in the expression $R_H= A/en$, except for the sample with particle sizes ~$2 \cdot 10^5$ nm, where e - electron charge.

During the extrusion of nanostructured samples of the $Bi_{0,85}Sb_{0,15}$ solid solution, due to plastic deformation, most of the polycrystal particles are oriented so that their trigonal axis becomes parallel to the extrusion axis, i.e. texture is formed. During plastic deformation, various crystal lattice defects simultaneously appear in individual particles. The degree of texture in nanostructured samples will depend on the technological parameters of the extrusion process, the size of particles (nanoparticles) and post-extrusion heat treatment. During heat treatment, disorientation of particles may also occur due to thermal energy, i.e. change in the degree of texture of the extruded sample [14].

The most considerable change in the degree of texture during annealing occurs in nanostructured samples with the smallest particle sizes. With increasing particle sizes in bulk nanostructured samples, the effect of heat treatment on the degree of texture is weakened. Defects associated with boundaries between crystallites (particles) lead to the fact that samples with minimal particle sizes (~ 15 nm) have a high concentration of current carriers among the studied samples. 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. 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 in the sample.

From Fig. 2 it can be seen that as the particle size decreases, the magnetoresistance of the samples decreases. For all samples with heat treatment, the value of magnetoresistance increases significantly.



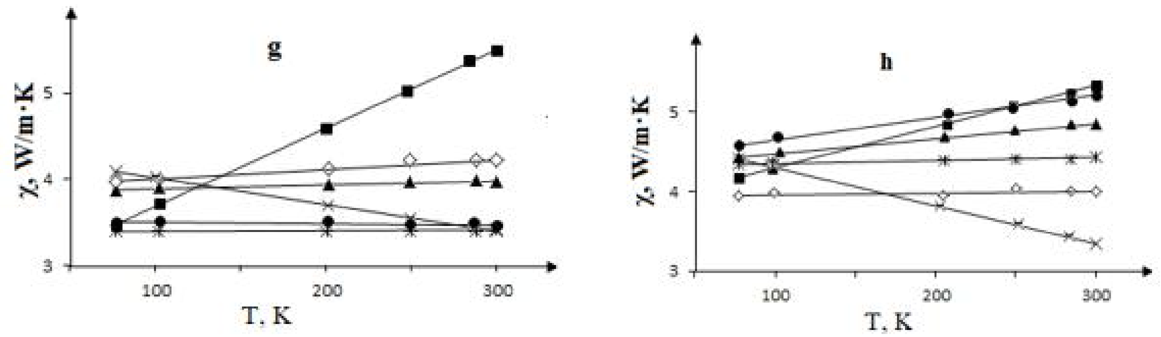


Fig. 1. Temperature dependences of the coefficients of electrical conductivity (σ), thermo-emf (α), Hall (R_H) and thermal conductivity (χ) of extruded samples of the $Bi_{0,85}Sb_{0,15}$ solid solution with different particle sizes that have not undergone heat treatment (a,c,e,g) and have undergone heat treatment (b,d,f,h). Curves 1-6 refer to samples with particle sizes - $2{\cdot}10^5$; 950; 650; 380; 30 and 15 nm, respectively.

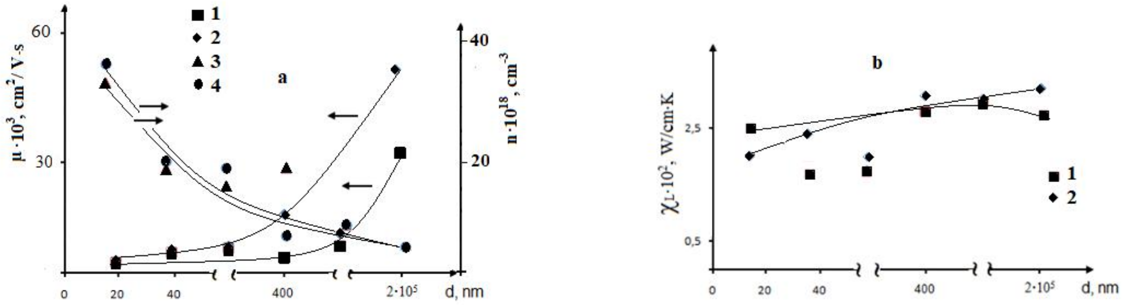
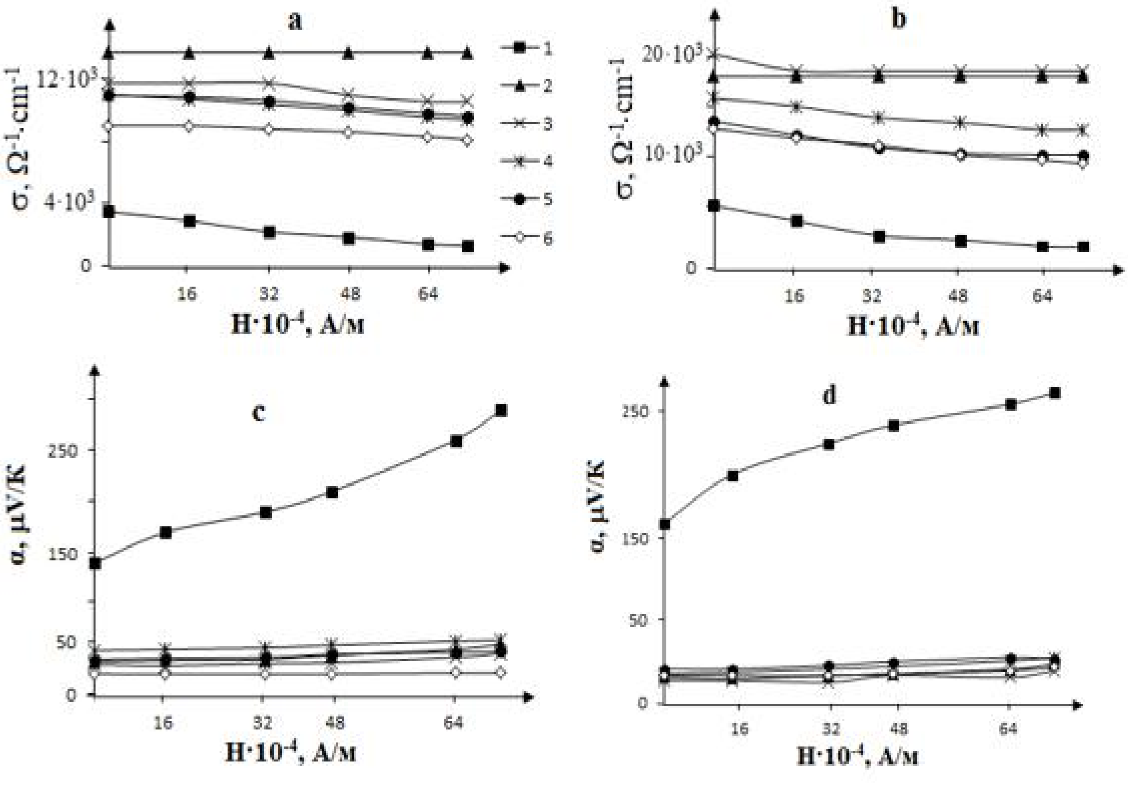


Fig. 2. Dependences of the concentration (n), mobility (μ) of current carriers (a) and the phonon part of thermal conductivity (χ_L) (b) of nanostructured extruded samples of the $Bi_{0,85}Sb_{0,15}$ solid solution on the particle size at ~77 K. Fig. a, curves 1,3 - unannealed samples, 2,4 - annealed samples, Fig. b- 1- annealed samples, 2- unannealed samples.



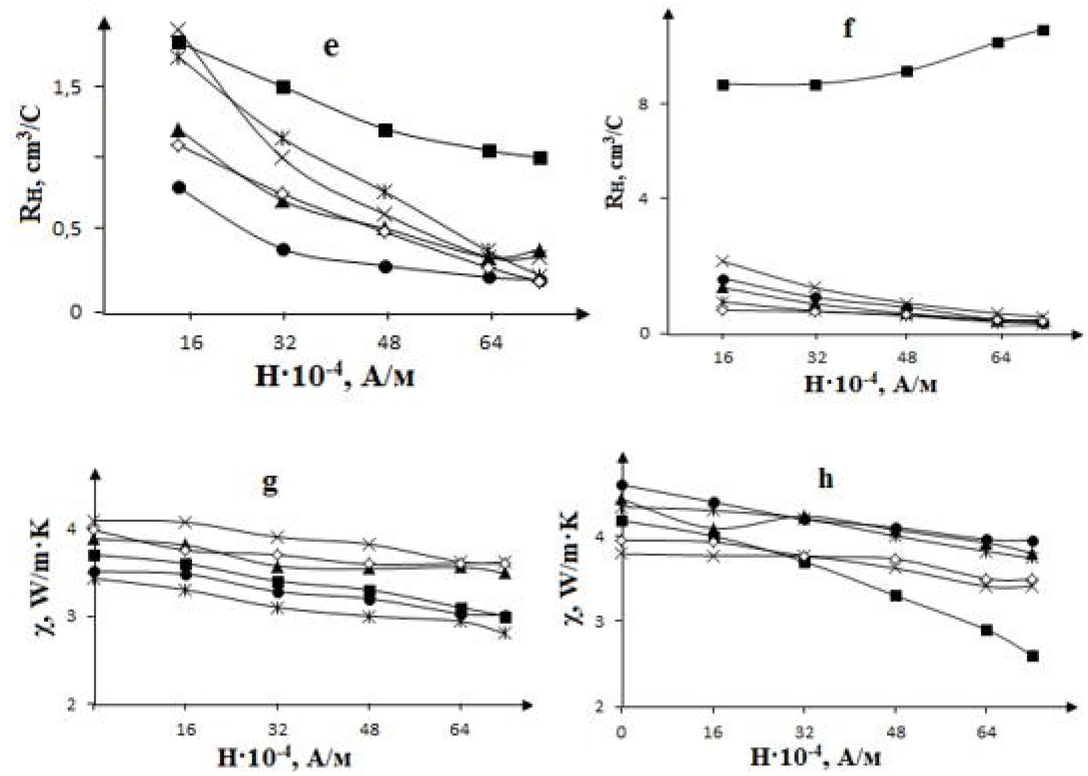


Fig. 3. Dependences of electrical conductivity (σ), thermo-e.m.f. (α),Hall (R_H) and thermal conductivity (χ) coefficients of the extruded samples of $Bi_{0,85}Sb_{0,15}$ solid solution with various sizes of particles before (a, c, e, g) and after (b, d, f, h) heat treatment on magnetic fields intensity at ~77 K. The designations are the same as in Fig.1

At ~77K, the dependences of α on the magnetic field strength for the studied samples with and without heat treatment are identical and almost independent of H, except for the sample with particle sizes ~$2 \cdot 10^5$ nm (Fig. 2).

In a magnetic field, some redistribution of the roles of various carriers in the total current in the sample occurs. The contribution of weakly scattering current carriers to the total current decreases due to an increase in the resistance to their movement, which, with a constant total current, leads to an increase in the contribution of strongly scattering particles. In this case, the average energy of current carriers changes. During heat treatment, scattering by acoustic phonons begins to prevail in 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 α 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 (~77 K), the dominant role is played by texture, and electrons are mainly scattered by structural defects. As the size of grains (nanoparticles) increases, the concentration of structural defects formed during plastic deformation decreases, which leads to a decrease in the electron concentration n, χ_e, an increase in μ, and a slight increase in χ_L.

During heat treatment, partial destruction of the texture and "healing" of structural defects occurs [13], which leads to a decrease in n and an increase in μ, σ and χ_L.

The nature of the dependence of electrical and thermal parameters on the magnetic field strength for both unannealed and annealed samples remains the same at ~300K. However, at ~300K the influence 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 $Bi_{0,85}Sb_{0,15}$ solid solution on grain sizes and heat treatment show that the dominant role in the scattering of current carriers and phonons in samples at ~77K is played by particle sizes, defects associated with boundaries between particles, and the degree of ordering (texture) of particles during extrusion, recrystallization and disorientation of crystallites during heat treatment. Heat treatment leads to a decrease in n and an increase in μ, χ, χ_e and magnetoresistance. With an increase in particle size, due to an increase in the energy required for particle orientation, the degree of texture in samples during deformation decreases, which leads to a weakening of the dependence of χ_p on particle size. The change in thermal parameters is satisfactorily explained by the changes occurring in the structure of the samples during extrusion and heat treatment which correlates with the changes occurring in the electrical parameters during these processes.

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