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MAGNETO-THERMOELECTRIC PROPERTIES OF $Bi_{85}Sb_{15}$ SOLID SOLUTION DOPED WITH LEAD AND TELLURIUM IMPURITIES

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Abstract- Extruded materials based on $Bi_{85}Sb_{15}$ compositions with ~630 μm grain sizes, doped with acceptor (Pb) and donor (Te) atoms were obtained, their thermo- and magnetothermoelectric properties in the range of ~77-300 K and at magnetic field intensity (H) up to ~74×10^4 A/m were studied. It was shown that by doping extruded samples of the $Bi_{85}Sb_{15}$+0.01 at.% Pb solid solution using Te atoms as donor impurities, the acceptor atoms of lead are initially compensated, and then with increasing content of tellurium atoms, Seebeck coefficient increases and approaches to Seebeck coefficient for non-doped solid sample $Bi_{85}Sb_{15}$ solution. The magnetic field influence on the parameters σ, α, R_h, χ for all studied annealed $Bi_{85}Sb_{15}$ samples is much stronger than in the same samples that did not pass annealing. For samples with a tellurium concentration of more than 0.005 at.%, at ~77 K the Seebeck coefficient for samples that have not been annealed and annealed is almost independent of the magnetic field strength. The magnetic field mainly effects on electronic component of the thermal conductivity of the studied samples reducing its value.

Keywords: Solid Solution, Extrusion, Quality Factor, Electrical Conductivity, Impurity.

1. INTRODUCTION

The widespread use of thermoelectric energy converters is limited by the relatively low thermoelectrics efficiency of materials used [1-4]. Single crystals on the base of Bi-Sb systems solid solutions have a record thermo- and magneto-thermoelectric efficiency at ~77÷150 K temperature range and therefore are widely used to create various energy converters and are promising materials in this direction [5-8]. In addition, Bi-Sb alloys are a model material that can be used to model the possibility of increasing the grain sizes of materials. However, due to the layered structure, single crystals of Bi-Sb systems have low mechanical strength, which limits their use [9, 10].

The extrusion method [11-17] allow to increase durability of thermoelectric, preserving high thermoelectric efficiency. The method has great productivity and opens up great opportunities for profiling thermoelement branches.

The thermoelectric efficiency of thermoelectrics is given as $Z=\alpha^2\sigma/\chi$, where σ is the electrical conductivity, α is Seebeck coefficient, χ is the thermal conductivity coefficient. The number of ways to maximize the quality factor Z is not so great. If we do not consider methods for suppressing the phonon component of thermal conductivity, which are well known [9] have already been implemented in most thermoelectrics, therefore, in recent years optimization has been carried out by varying the current carriers density in the materials used.

In case of one type of the charge carriers, an increase in the electron concentration by the introduction of one type of impurities, increasing the electrical conductivity, while reduces Seebeck coefficient and a decrease in the concentration leads to a reverse direction of variation of these parameters. Simultaneously introduced impurities still contribute to a decrease in the mobility of current carriers, which negatively affects the efficiency of the thermoelectric material. Therefore, to obtain a thermoelectric material with the necessary parameters, one should not only establish the optimal composition of the material, but also dope it with various types of impurities, i.e., to carry out complex doping, which ensures the optimal concentration of charge carriers and carriers scattering conditions, leading to a sufficiently high ratio of mobility to the phonon heat conduction μ/χ_{ph}, and to develop production and heat treatment technologies for this composition.

Extruded samples of $Bi_{85}Sb_{15}$ composition have a high factor of merit Z at a temperature ~77 K [18]. Further optimization of their kinetic coefficients can be achieved by joint doping with acceptor and donor impurities. An analysis of the literature shows that there are very few such works, and there is no work on the study of the effect of the magnetic field intensity on electrical and thermal properties of these systems.

Thermo-, as well as magneto-thermoelectric coolers on the base of Bi-Sb systems solid solutions are widely used in various fields of electronics. Therefore, studies of the magneto-thermoelectric properties of Bi-Sb systems solid solutions with various types of impurities and the creation of low-temperature electronic coolers based on them are of certain scientific and practical interest.

In order to create a material suitable for practical use for energy converters based on solid solutions of $Bi_{85}Sb_{15}$ systems, in this work we obtained extruded materials based on $Bi_{85}Sb_{15}$ compositions doped with acceptor (Pb) and donor (Te) atoms with grain sizes of ~630 μm and studied their thermo- and magneto-thermoelectric properties in the range of 77-300 K and with magnetic field intensities (H) till ~74×10^4 A/m.

2. EXPERIMENTAL TECHNIQUE

$Bi_{85}Sb_{15}$ composition was synthesized by direct fusion of the components in the corresponding stoichiometry in a quartz ampoule, previously etched in a solution of nitrohydrochloric acid and washed with distilled water. The ampoule was pumped out to a residual pressure of ~10^{-2} Pa and was sealed off. As the initial materials "Bi-000" brand bismuth and "Sb-0000" brand antimony were used. The synthesis was made at ~673 K for 2 hours. For good homogenization of the alloy, the ampoule furnace was rocked. Then the substance was cooled to room temperature by lowering the ampoule into water. The impurities and initial components were weighed with an accuracy of ±0.0001 g. The dopants lead and tellurium were entered in the process of synthesis. Specimens with a low concentration of tellurium were obtained by fusion of the sample with a concentration of 0.1 at.% Te with a sample of $Bi_{85}Sb_{15}$ doped with 0.01 at.% Pb.

From powders of $Bi_{85}Sb_{15}$ solid solution with dimensions ~630 μm briquettes with a diameter of ~30 mm, suitable for extrusion were pressed. This process was conducted at ~300 K and a pressure ~3.5 T/cm^2. The extrusion process was conducted on MS-1000 hydraulic press from a diameter 30 mm to a diameter of 6 mm using special equipment. The parameters of the extrusion process (temperature, pressure, drawing speed, etc.) were selected so that the creating of the rods took place passed in superplastic conditions without any macro- and micro-disturbances.

Samples for research in the shape of a parallelepiped with 3×5×12 mm dimensions were cut from extruded rods using the method of electric spark cutting. The disturbed layer generated on the specimen surfaces, when cutting, was disposed using electrochemical etching in a solution of $KOH+C_4H_4O_6+H_2O$. The specimens were thermally treated in quartz ampoules pumped out to ~0.1 Pa at ~503 K during two hours.

Electrophysical characteristics were determined by the method described elsewhere [19] along the length of the sample, i.e., in the direction of extrusion. We studied specimens that did not passed heat treatment extrusion and the same specimens passed heat treatment at ~503 K for 2 hours in vacuum. The electrical conductivity (σ), Seebeck (α), Hall (R_h) coefficients and χ in ~77-300 K range and with magnetic field intensity (H) till to ~74×10^4 A/m were studied.

3. RESULTS AND DISCUSSION

There are presented in Figures 1-4 and in Table 1 results of the measurement results. Figures show that the effect of the magnetic field on the parameters σ, α and R_h in the heat treated specimens is stronger than in the specimens without heat treatment. As concentration of tellurium increases, the density of current carriers increases, and effect of the magnetic field on α of the samples not annealed and annealed is weakened.

When the extruded samples of $Bi_{85}Sb_{15}$+0.01 at.% Pb are doped by tellurium donors, at first (till 0.0001 at.% Te) acceptor Pb are compensated, after increasing in electron density, that is growth in σ and a decreasing of absolute values of α and R_h is observed.

After annealing, the Hall coefficient for all samples increases at ~77 K, and up to 0.0005 at.% Te Seebeck coefficient increases. With an increase of the content of tellurium in the sample, Seebeck coefficient decreases.

During extrusion simultaneously with the formation of texture owing to plastic deformation in the samples, the formation of structural defects occurs [20]. They play role of scattering centers for current carriers and decrease their mobility. At the same time, an increase in the density of current carriers occurs, associated with the formation on defects of electrically active centers. During heat treatment, the structure normalizes, i.e. as if "healing" of structural defects occurs

In non-doped samples insignificant effect of annealing on α with a significant change in σ shows that during heat treatment mainly the mobility of charge carriers changes, i.e., the concentration of scattering centers decreases. Moreover, these changes are especially evident at low temperatures (~77 K), where the role of impurity conductivity and electron scattering by defects prevails. In samples subjected to heat treatment, the concentration of structural defects is low, and therefore, scattering by acoustic phonons predominates at low temperatures. Therefore, in $Bi_{85}Sb_{15}$ samples at low temperatures α grows strongly in a magnetic field.

The increase in R_h at ~77 K after heat treatment is apparently mainly due to a change in the parameter A in the expression $R_h=A/en$ [21]), which characterizes the scattering mechanism.

In samples that did not undergo heat treatment at a temperature of 77 K, defect scattering prevails in electron scattering. A small change in α during heat treatment suggests that these defects are mainly non-ionized. With heat treatment, the concentration of structural defects decreases. This manifest itself in growth in the mobility of current carriers, as well as in electrical conductivity. The proposed mechanism is also supported by data on the dependence of the electrical properties of $Bi_{85}Sb_{15}$ extruded specimens on the magnetic field intensity.

The effect of magnetic field on parameters σ, α and R_h in thermally treated specimens is much stronger than in the samples that have not undergone heat treatment. At ~77 K the Seebeck coefficient in samples, in which tellurium concentration is more than 0.005 at.%, which did not pass annealing and pass annealing, is almost independent of the magnetic field strength.

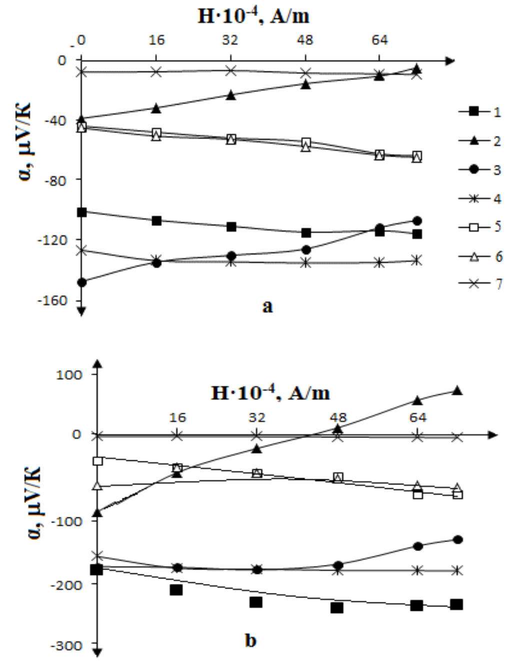

Figure 1. Seebeck coefficient of $Bi_{85}Sb_{15}$ extruded specimens versus magnetic field intensity at ~77 K. Curves 1- refer to pure sample; 2- to specimens of $Bi_{85}Sb_{15}$+0.01 at.% Pb and 3-7 - to samples 0.0001 at.% Te; 0.0005 at.% Te; 0.005 atom% Te; 0.01 at.% Te; 0.1 at.% Te, respectively, a- non-annealed, b- annealed samples

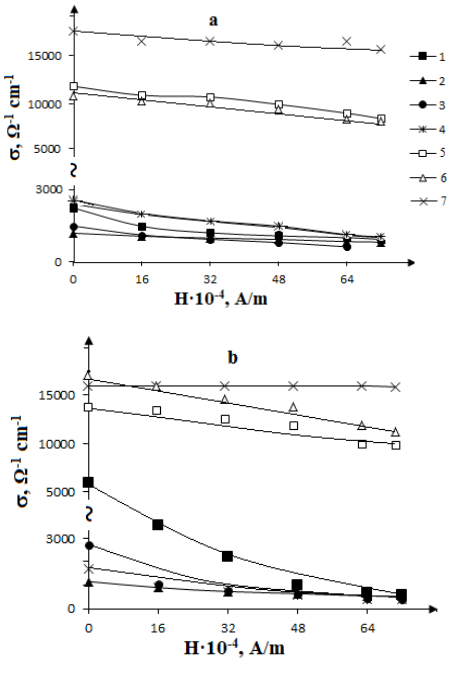

Figure 2. The electrical conductivity of the extruded $Bi_{85}Sb_{15}$ specimens versus on the magnetic field intensity at ~77 K, designations are the same as in Figure 1

In annealed samples with 0.01 at.% Pb at ~77 K at a magnetic field strength of ~42×10^4 A/m, the type of the conductivity changes from electronic to hole type. Non-doped and tellurium-doped samples at ~77 K have n-type conductivity in all the investigated range of magnetic field strengths.

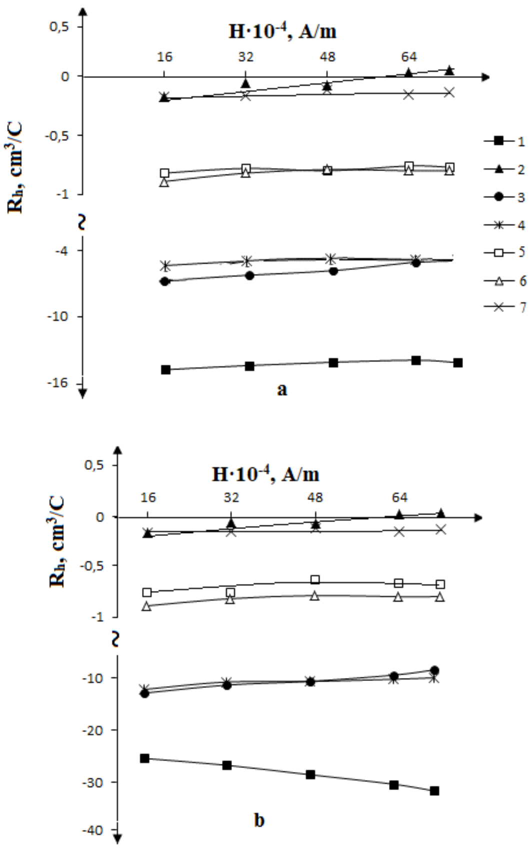

Figure 3. The Hall coefficient for the extruded $Bi_{85}Sb_{15}$ specimens versus magnetic field intensity at ~77 K, designations are the same as in Figure 1

The Hall coefficient of the same samples that passed and did not pass annealing at ~77 K changes the type of conductivity at high values of the magnetic field strength. At high temperatures, change in α under a magnetic field is almost same for annealed and non-annealed samples.

Magnetic field differently influences on electrical conductivity of samples having n- and p-type conductivity is different. In the case of the n-type, the magnetoresistance in samples after heat treatment is always greater than in samples that have not undergone heat treatment [22].

If magnetic field is applied to specimen perpendicular to direction of electron motion, the charge carriers are deflected by the Lorentz force. In this case, carriers that are less scattering and have, therefore, longer mean free path in a magnetic field are more deflected more than strongly scattering carriers.

In samples without heat treatment, at low temperatures scattering of electrons and holes by structural defects predominates, to which slow current carriers are subject to a large degree. Therefore, the magnetic field mainly rejects carriers with high energy and their contribution to the total current decreases. Consequently, the average carrier energy decreases. Due to the fact that at low temperatures (~77 K) the total number of current carriers with high energy is small, the effect of H on medium-energy carriers and, therefore, on α is insignificant.

At high temperatures, the average energy of the current carriers grows, and scattering by the acoustic vibrations of the lattice begins to prevail, which fast carriers are more susceptible to than slow ones. Therefore, at high temperatures, when the sample is placed in a magnetic field, the contribution to the total current of fast carriers increases, therefore, the average energy of charge carriers in the $Bi_{85}Sb_{15}$ sample grows, and as a result, α increases.

The magnetic field mainly affects on electron part of thermal conductivity. Therefore, the total thermal conductivity in a magnetic field does not change significantly.

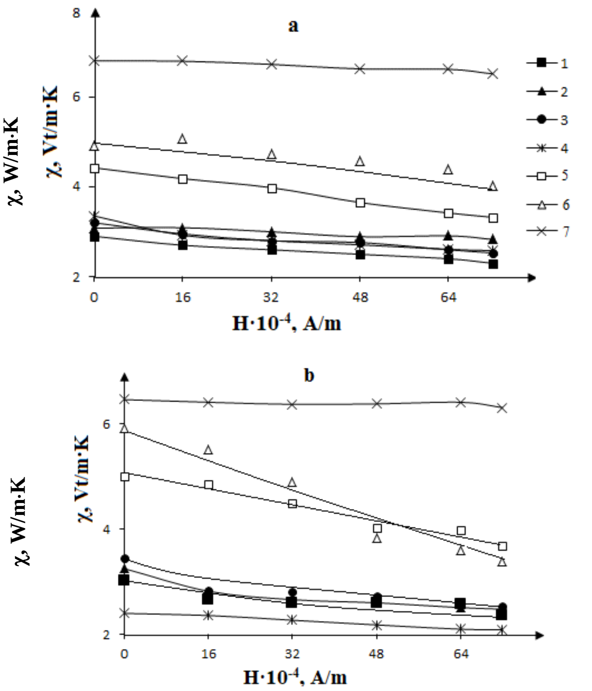

Figure 4. The thermal conductivity coefficient for $Bi_{85}Sb_{15}$ for extruded specimens versus magnetic field intensity at ~77 K, designations are the same as in Figure 1

Table 1. Dependences of electric conductivity (σ), Seebeck (α) and Hall (R_h), thermal conductivity (χ) coefficients, charge carrier mobility (μ) and charge carrier concentration (n) at ~77 K on tellurium concentration

No	At 77 K temperature					
	Non-annealed samples					
	σ, Ω^{-1} cm^{-1}	α, μV/K	R_h, cm^3/C	χ, W/m·K	μ, cm^2/ V·s	n, cm^{-3}
1	2393	-173	-14.83	2.9	35488	0.4×10^{18}
2	1273	-40	-0.69	3.08	878	9.1×10^{18}
3	1591	-148	-7.4	3.05	11773	0.8×10^{18}
4	2750	-127	-6.71	3.05	18453	0.9×10^{18}
5	11823	44.1	-0.69	4.42	8158	9.1×10^{18}
6	10823	-45.3	-0.45	4.92	4870	13.9×10^{18}
7	17506	-7.9	-0.23	6.8	4026	27.2×10^{18}
Annealed samples						
1	5387	-178	-25.3	3.02	136291	0.25×10^{18}
2	1462	-89.6	-4.33	3.04	6331	1.4×10^{18}
3	2020	-171	-11.1	3.03	22422	0.56×10^{18}
4	1604	-154	-10.6	2.39	17002	0.58×10^{18}
5	13752	-30.3	-0.72	5	9901	0.7×10^{18}
6	17026	-56.7	-0.69	5.3	11748	9.1×10^{18}
7	15600	-3.3	-0.1	6.45	1560	62.5×10^{18}

Note: 1- non-doped sample; 2- samples $Bi_{85}Sb_{15}$+0.01 at.% Pb; 3- $Bi_{85}Sb_{15}$+0.01 at.% Pb+0.0001 at.% Te; 4÷7 - $Bi_{85}Sb_{15}$+0.01 at.% Pb+0.0005 at.% Te; $Bi_{85}Sb_{15}$+0.01 at.% Pb+0.005 at.% Te; $Bi_{85}Sb_{15}$+0.01 at% Pb+0.01 at% Te; $Bi_{85}Sb_{15}$+0.01 at.% Pb+0.1 at.% Te, respectively

4. CONCLUSION

By doping the extruded $Bi_{85}Sb_{15}$+0.01 at% Pb samples with Te donor atoms, acceptor atoms of lead are initially compensated, and then with increase of tellurium content, the Seebeck coefficient increases and approaches to one of the non-doped $Bi_{85}Sb_{15}$ solid solution sample.

The influence of the magnetic field on the parameters σ, α, R_h, χ of all studied annealed $Bi_{85}Sb_{15}$ samples is much stronger than in the samples that did not pass annealing in the same samples. For samples with a tellurium concentration of more than 0.005 at.%, at ~77 K, the Seebeck coefficient for samples that have not been annealed and annealed is almost independent of the magnetic field intensity. The magnetic field mainly reduces the electron part of thermal conductivity of studied samples.

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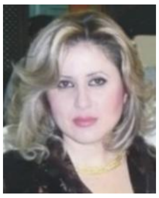
BIOGRAPHIES

Mayil Masim Tagiyev was born in Azerbaijan on April 11, 1959. He is a Doctor of Sciences in Physics. Currently, he is a Professor of Azerbaijan State Economic University, Baku, Azerbaijan. Since 1982 he is engaged in development of extrusion mode for various semiconductor systems and extrusion installations, preparation of initial extrusion samples and investigation their thermoelectric properties. His research interests are in the area of preparation and research of high-effective thermoelectric materials on the basis of bismuth- stibium solid solutions for thermoelectric energy converters. His publications are more 270 articles and 7 monographs and manuals.



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