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Magnetothermoelectric Properties of Extruded $Bi_{85}Sb_{15}\langle Pb,Te\rangle$

M. M. Tagiyev[a, b, *]

[a] *Azerbaijani State University of Economics, Baku, AZ 1001 Azerbaijan*
[b] *Institute of Physics, Academy of Sciences of Azerbaijan, Baku, AZ 1141 Azerbaijan*
**e-mail: mail_tagiyev@mail.ru*

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Abstract—$Bi_{85}Sb_{15}$ + 0.01 at % Pb materials have been synthesized and their electrical conductivity σ, thermoelectric power α, Hall coefficient R_H, and thermal conductivity χ have been measured as functions of temperature and magnetic field. Additional doping with up to 0.1 at % tellurium donor has been shown to compensate for the Pb acceptor effect, leading to an increase in electron concentration in the samples. As a result, σ and α approach those of $Bi_{85}Sb_{15}$ free of Pb impurities. Heat treatment partially eliminates structural defects, leading to an increase in carrier mobility and lattice thermal conductivity.

Keywords: extrusion, annealing, combined doping, impurity, electrical conductivity

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INTRODUCTION

Wide use of thermoelectric energy converters is limited by the relatively low thermoelectric figure of merit of the materials suitable for this application. Single crystals based on solid solutions in the Bi–Sb system offer record high thermoelectric and magnetothermoelectric figures of merit at low temperatures, which makes them promising thermoelectric materials. However, they have low mechanical strength, associated with the layered nature of their crystal structure, which limits their potential application field [1–4]. One effective way to improve their mechanical strength, while maintaining sufficiently good thermoelectric performance, is extrusion [5–10]. The method offers a high production rate and opens up wide possibilities for shaping legs of thermoelectric generators [11–14].

Thermoelectric efficiency of thermoelectric materials is determined by the parameter $Z = \alpha^2\sigma/\chi$, where σ is electrical conductivity, α is thermoelectric power, and χ is thermal conductivity. There are not many ways of maximizing the thermoelectric figure of merit. Without methods for suppressing the phonon contribution to thermal conductivity, which are well known [15], most thermoelectrics have already been put into practice, so in recent years optimization has reduced to varying carrier concentration in available materials [16]. To obtain a thermoelectric material with required parameters, it should be doped with various impurities so as to optimize carrier concentration and carrier scattering processes.

Donor and acceptor doping of $Bi_{88}Sb_{12}$ alloys allows carrier concentration to be tuned over a wide range [1, 5]. Small tellurium additions raise the electrical conductivity of the material and, according to calculations, are expected to increase the thermoelectric figure of merit of the $Bi_{88}Sb_{12}$ alloys, despite some decrease in the magnitude of their thermoelectric power. It has been shown that Z increases only at a doping level below 0.001 at % Te [5]. Further increase in tellurium dopant concentration leads to a decrease in Z, which is the result of the sharp drop in carrier mobility with increasing dopant concentration (increasing carrier concentration). Underrating of this circumstance underlies many theoretical predictions of an increase in Z in calculations of transport coefficients at constant carrier mobility [17–19].

It is reasonable to assume that transport coefficients can be optimized as well by codoping of extruded $Bi_{85}Sb_{15}$ samples with acceptor and donor impurities (combined doping).

As shown earlier [9, 20], extruded and annealed $Bi_{85}Sb_{15}$ samples having a grain size of ~630 μm and doped with Pb acceptor (0.01 at %) have a rather low 77-K electrical conductivity (σ = 1462 S/cm) and switch from *n*- to *p*-type in a magnetic field. For this reason, this material was chosen to study the effect of codoping with acceptor (Pb) and donor (Te) impurities on the magnetothermoelectric properties of samples.

The purpose of this work was to study the effect of combined doping with acceptor (Pb) and donor (Te) impurities on the magnetothermoelectric properties of $Bi_{85}Sb_{15}$ crystals with a grain size of ~630 μm at temperatures from ~77 to 300 K in magnetic fields (H) of up to ~74×10^4 A/m.

Table 1. Effect of tellurium dopant concentration on the electrical conductivity (σ), thermoelectric power (α), Hall coefficient (R_H), thermal conductivity (χ), carrier mobility (μ), and carrier concentration (n) of the extruded $Bi_{85}Sb_{15}$ + 0.01 at % Pb samples at ~77 K

Sample	σ, S/cm	α, μV/K	$R_H \times 10^{-8}$, cm^3/C	$\chi \times 10^2$, W/(cm K)	μ, $cm^2/(V s)$	$n \times 10^{-18}$, cm^{-3}	σ, S/cm	α, μV/K	$R_H \times 10^{-8}$, cm^3/C	$\chi \times 10^2$, W/(cm K)	μ, $cm^2/(V s)$	$n \times 10^{-18}$, cm^{-3}
	before heat treatment						after heat treatment					
1	2393	−173	−14.83	2.9	35488	0.4	5387	−178	−25.3	3.02	136291	0.25
2	1273	−40	−0.69	3.08	878	9.1	1462	−89.6	−4.33	3.04	6331	1.4
3	1591	−148	−7.4	3.05	11773	0.8	2020	−171	−11.1	3.03	22422	0.56
4	2750	−127	−6.71	3.05	18453	0.9	1604	−154	−10.6	2.39	17002	0.58
5	11823	44.1	−0.69	4.42	8158	9.1	13752	−30.3	−0.72	5	9901	0.7
6	10823	−45.3	−0.45	4.92	4870	13.9	17026	−56.7	−0.69	5.3	11748	9.1
7	17506	−7.9	−0.23	5.6	4026	27.2	15600	−3.3	−0.1	5.7	1560	62.5

(*1*) Undoped sample, (*2*) $Bi_{85}Sb_{15}$ + 0.01 at % Pb, (*3*) $Bi_{85}Sb_{15}$ + 0.01 at % Pb + 0.0001 at % Te, (*4*) $Bi_{85}Sb_{15}$ + 0.01 at % Pb + 0.0005 at % Te, (*5*) $Bi_{85}Sb_{15}$ + 0.01 at % Pb + 0.005 at % Te, (*6*) $Bi_{85}Sb_{15}$ + 0.01 at % Pb + 0.01 at % Te, (*7*) $Bi_{85}Sb_{15}$ + 0.01 at % Pb + 0.1 at % Te.

EXPERIMENTAL

$Bi_{85}Sb_{15}$ was synthesized via direct melting of the starting components. An appropriate mixture of the starting materials was placed in a silica ampule preetched in a chromic/sulfuric acid mixture and rinsed with distilled water. The ampule was then pumped down to a residual pressure of ~10^{-3} Pa and sealed off under vacuum. The starting materials used were Vi-000 bismuth and Su-0000 antimony. As dopants, we used T-sCh tellurium (distilled or twice sublimed) and Pb-000 lead. The dopants and constituent components were weighed with an accuracy of ±0.0001 g. The Pb and Te dopants were added during synthesis. Samples with low tellurium concentrations were prepared by melting appropriate amounts of $Bi_{85}Sb_{15}$ containing 0.1 at % Te and $Bi_{85}Sb_{15}$ doped with 0.01 at % Pb.

Synthesis was carried out at a temperature of ~673 K for 2 h. To properly homogenize the alloy, the furnace containing the ampule was constantly rocked. Next, the material was cooled to room temperature (by immersing the ampule in water).

The synthesized material was comminuted by grinding in a porcelain mortar and sieved to the size range ≤0.630 mm using a specially designed sieve.

$Bi_{85}Sb_{15}$ powders with a particle size of ~630 μm were pressed at room temperature and a pressure of ~350 MPa into compacts ~30 mm in diameter, convenient for extrusion. Extrusion was performed on an MS-1000 hydraulic press from a 30-mm to 6-mm diameter using purpose-designed accessories. The extrusion process parameters (temperature, pressure, ram speed, and others) were chosen so that the bars were formed under superplasticity conditions, without macro- or microdefects.

Samples for our measurements, in the form of a parallelepiped 3 × 5 × 12 mm in dimensions, were cut from the extruded rods by spark erosion using an A.207M machine. The cutting-induced surface damage layer was removed by electrochemical etching in a $KOH + C_4H_4O_6 + H_2O$ solution [21]. The extruded samples were annealed at ~503 K for 2 h in silica ampules pumped down to a pressure of ~10^{-3} Pa.

The electrical and thermal parameters of the samples were measured as described previously [22], along their length, that is, in the extrusion direction. We studied the extruded samples before and after annealing. We measured their electrical conductivity (σ), thermoelectric power (α), Hall coefficient (R_H), and thermal conductivity χ in the range ~77–300 K in magnetic fields (H) of up to ~74 × 10^4 A/m. The results are presented in Figs. 1–4 and Table 1.

RESULTS AND DISCUSSION

The low-temperature portion of the $\sigma(T)$ curve for the extruded undoped $Bi_{85}Sb_{15}$ samples points to an increase in carrier concentration (n) with temperature. The high-temperature $\sigma(T)$ behavior is determined largely by the temperature dependence of carrier mobility [6].

As shown earlier using temperature-dependent σ and α data [23], Pb-doped $Bi_{0.85}Sb_{0.15}$ samples contain two types of donor levels: shallow (0.01 eV) and deep (0.04 eV). The electrical properties of the undoped samples are determined largely by the shallow donor

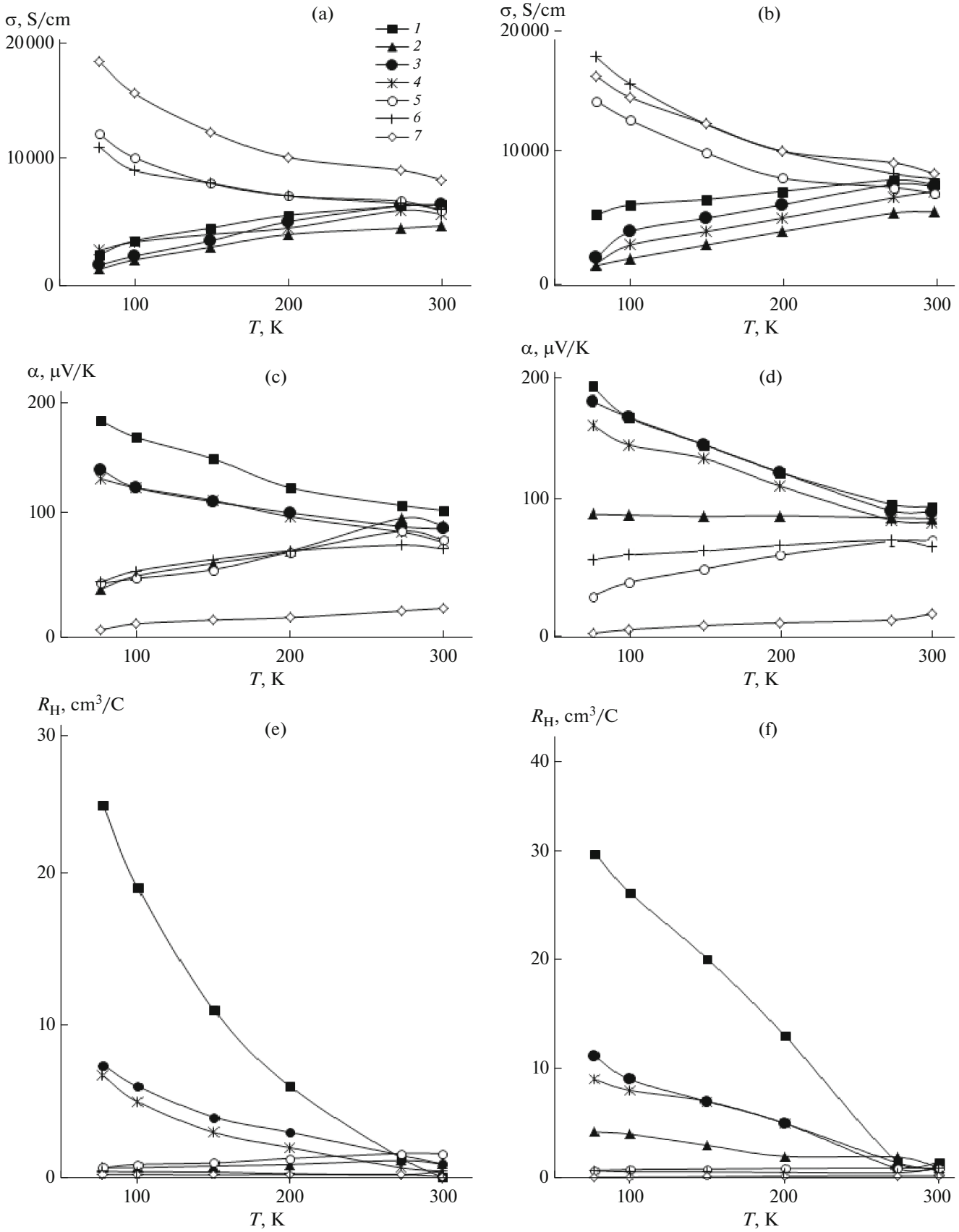

Fig. 1. Temperature dependences of the (a, b) electrical conductivity, (c, d) thermoelectric power, and (e, f) Hall coefficient for the extruded $Bi_{85}Sb_{15}$ samples (a, c, e) before and (c, d, f) after heat treatment; curves *1*–*7* correspond to the samples in Table 1.

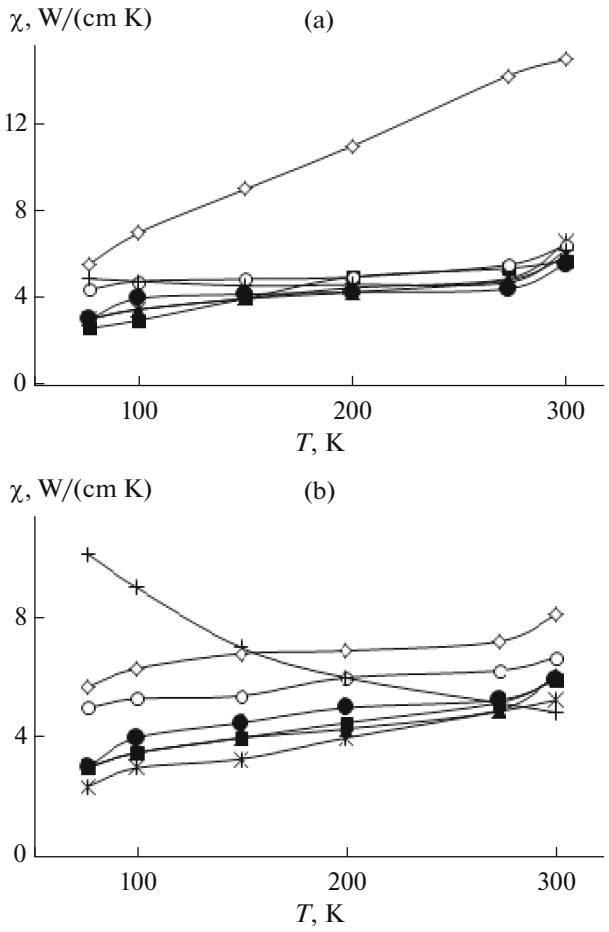

Fig. 2. Temperature dependences of thermal conductivity (χ) for the extruded $Bi_{85}Sb_{15}$ samples (a) before and (b) after heat treatment; the same designations as in Fig. 1.

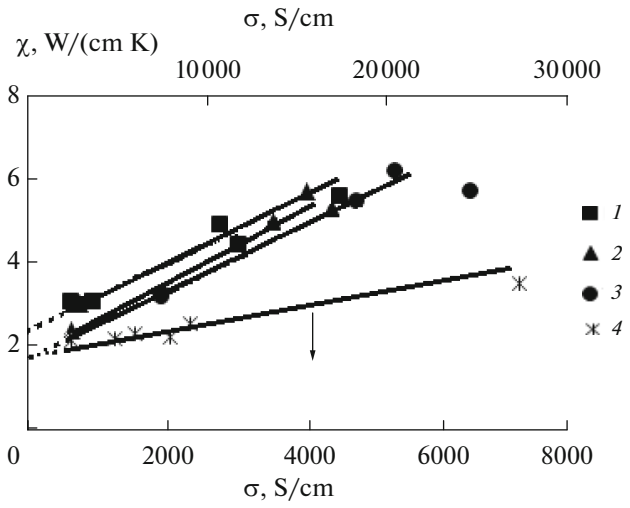

Fig. 3. Thermal conductivity (χ) vs. electrical conductivity (σ) at ~77 K for the extruded $Bi_{85}Sb_{15}$ samples: (*1*, *2*) codoped samples before and after annealing, respectively; (*3*) annealed samples doped with 0.0001, 0.0005, 0.001, 0.01, and 0.1 at % Te; (*4*) annealed samples doped with 0.001, 0.005, 0.01, 0.05, 0.075, and 0.1 at % Pb.

levels, and the Pb dopant compensates them. In the samples containing 0.01 at % Pb, the shallow levels are fully compensated, so σ drops to a minimum. With increasing temperature, the ionization of the deep donor levels in this sample increases and, as a consequence, its σ rises with temperature, approaching the σ of the undoped sample in the range from 200 to 300 K. Increasing the Pb concentration leads to compensation of the deep donor levels and produces new shallow acceptor levels. As a result, the samples containing 0.05 at % Pb and more have *p*-type conductivity at a temperature of ~77 K [9, 20].

Both before and after heat treatment, the total thermal conductivity χ of the extruded $Bi_{85}Sb_{15}$ + 0.01 at % Pb samples at ~77 K is a nonmonotonic function of tellurium content. With increasing tellurium concentration, the thermal conductivity of the codoped samples increases.

The total thermal conductivity of the samples at ~77 K is contributed by the lattice (χ_l) and electron (χ_e) components:

$$\chi = \chi_l + \chi_e = \chi_l + L\sigma T, \quad (1)$$

where $L = A(k/e)^2$ is the Lorenz number (here k is Boltzmann's constant and e is the electron charge). A was evaluated from the dependence of A on thermoelectric power [24].

As shown earlier [25], the electrical conductivity of extruded $Bi_{85}Sb_{15}$ samples with a low concentration of electrically active impurities (N) changes by several times, whereas their lattice thermal conductivity remains almost constant. Then, we have

$$\chi(N) = \chi_l + \chi_e(N) = \chi_l + L\sigma(N)T. \quad (2)$$

Extrapolating the plot of χ against σ to σ = 0, we can find the lattice thermal conductivity of the samples (Fig. 3).

The addition of Pb and Te electrically active impurities to the extruded $Bi_{85}Sb_{15}$ samples can change L as well. However, calculations show that this change is insignificant (~10%) compared to the change in σ (by a factor of ~3.7). This leads us to conclude that the variation in the total thermal conductivity of the codoped $Bi_{85}Sb_{15}$ solid solutions is dominated by the electron thermal conductivity χ_e.

In addition, the electrical and thermal conductivities of the $Bi_{85}Sb_{15}$ samples were measured as functions of magnetic field and the $\sigma(H)$ and $\chi(H)$ data were used to determine χ_l. The χ_l values obtained from measurements in a magnetic field and those calculated from the $\chi(\sigma)$ data agree well.

The α and R_H of the $Bi_{85}Sb_{15}$ samples doped with 0.01 at % Pb and annealed in zero magnetic field do not change sign with temperature. At ~77 K, increas-

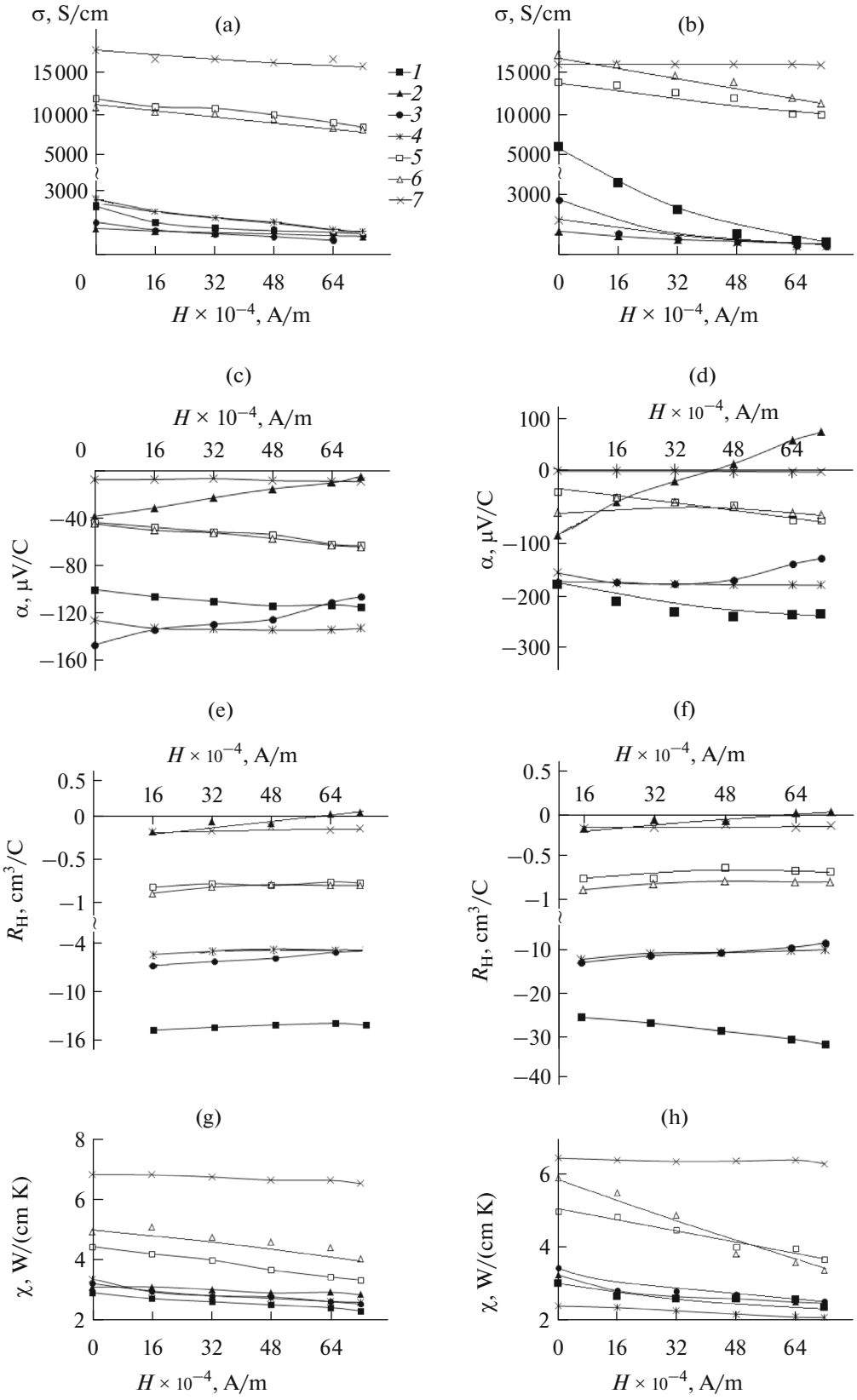

Fig. 4. (a, b) Electrical conductivity, (c, d) thermoelectric power, (e, f) Hall coefficient, and (g, h) thermal conductivity as functions of magnetic field at ~77 K for the extruded $Bi_{85}Sb_{15}$ samples (a, c, e, g) before and (c, d, f, h) after annealing; curves *1*–*7* correspond to the samples in Table 1.

ing the magnetic field strength changes the sign of α and R_H from negative to positive (Figs. 4d, 4f, curves *2*, respectively). The magnetic-field-induced type inversion in the $Bi_{85}Sb_{15}$ samples doped with 0.01 at % Pb can be accounted for by the fact that electrons and holes differ in mobility ($\mu_e > \mu_h$).

Annealing increases the 77-K Hall coefficient of all the $Bi_{85}Sb_{15}\langle Pb,Te\rangle$ samples (except $Bi_{85}Sb_{15}$ + 0.01 at % Pb + 0.1 at % Te) and the 77-K α of the samples containing up to 0.0005 at % Te. At Te concentrations above 0.0005 at %, the thermoelectric power decreases.

Because of the decrease in carrier mobility, the magnetic field has a weaker effect on the electrical parameters of the annealed and unannealed samples at high temperatures (~300 K).

During extrusion, plastic deformation produces not only texture of the samples but also structural defects [26]. The defects act as carrier scattering centers, reducing carrier mobility. Concurrently, the formation of electrically active centers at defects leads to an increase in carrier concentration. Heat treatment partially eliminates structural defects. The insignificant effect of annealing on the α of the undoped samples, in combination with considerable changes in σ, indicates that heat treatment influences predominantly carrier mobility, that is, it reduces the concentration of carrier scattering centers (Fig. 1, Table 1). These changes are especially obvious at low temperatures (~77 K), where extrinsic conduction and electron scattering by defects play a key role. In the annealed samples, the density of structural defects is low, and at low temperatures scattering by acoustic phonons prevails. Because of this, an applied magnetic field causes a large increase in the low-temperature α of the undoped samples, and the magnetic field has a much stronger effect on the electrical parameters of the annealed samples in comparison with the unannealed samples.

The heat treatment-induced increase in R_H at ~77 K seems to be mainly due to changes in the parameter A, which characterizes the scattering mechanism in the relation $R_H = A/en$, where e is the electron charge and n is carrier concentration.

Because of the difference in mobility between electrons and holes in $Bi_{85}Sb_{15}$, an applied magnetic field has different effects on the electrical conductivity of n- and p-type samples. Heat treatment always increases the magnetoresistance of the n-type samples.

CONCLUSIONS

Extruded $Bi_{85}Sb_{15}$ samples containing 0.01 at % lead acceptor and additionally doped with 0.1 at % tellurium donor have been prepared and their electrical conductivity σ, thermoelectric power α, Hall coefficient R_H, and thermal conductivity χ have been investigated in the range ~77–300 K in magnetic fields (H) up to ~74×10^4 A/m. We have calculated carrier concentration n, carrier mobility μ, electron thermal conductivity χ_e, and lattice thermal conductivity χ_l in the samples.

Compensating for the Pb acceptor effect, tellurium impurities lead to an increase in electron concentration in the samples. As a result, σ and α approach those of $Bi_{85}Sb_{15}$ free of Pb impurities.

Carrier mobility (and hence electrical parameters and electronic thermal conductivity) and lattice thermal conductivity in the samples are significantly influenced by structural defects, which can be eliminated by heat treatment. As the temperature is raised, phonon scattering by structural defects and impurity centers becomes weaker.

CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

REFERENCES

1. Zemskov, V.S., Belaya, A.D., Roslov, S.A., et al., Thermoelectric properties of Bi–Sb solid solutions, *Izv. Akad. Nauk SSSR, Met.,* 1978, no. 1 pp. 73–76.
2. Luk'yanova, L.N. and Kutasov, V.A., Galvanomagnetic and thermoelectric properties of multicomponent *n*-Type solid solutions based on Bi and Sb chalcogenides, *Phys. Solid State,* 2006, vol. 48, no. 4, pp. 647–653.
3. Grabov, V.M., Komarov, V.A., and Kablukova, N.S., Galvanomagnetic properties of thin films of bismuth and bismuth–antimony alloys on substrates with different thermal expansions, *Phys. Solid State,* 2016, vol. 58, no. 3, pp. 622–628. https://doi.org/10.1134/S1063783416030136
4. Yim, W.H. and Amith, A., Bi–Sb Alloys for Magnetothermoelectric and thermo-magnetic cooling, *Solid State Electron.,* 1972, vol. 10, no. 10, pp. 1141–1165.
5. Banaga, M.P., Sokolov, O.B., Benderskaya, T.E., Dudkin, L.D., Ivanova, A.B., and Fridman, I.I., Structure and thermoelectric properties of extruded $Bi_{0.88}Sb_{0.12}$, *Izv. Akad. Nauk SSSR, Neorg. Mater.,* 1986, vol. 22, no. 4, pp. 619–622.
6. Tagiyev, M.M., Agaev, Z.F., and Abdinov, D.Sh., Thermoelectric properties of extruded $Bi_{85}Sb_{15}$, *Inorg. Mater.,* 1994, vol. 30, no. 3, pp. 356–358.
7. Tagiyev, M.M., Samedov, F.S., and Agaev, Z.F., High-temperature extruded $Bi_{0.85}Sb_{0.15}$-based material for low-temperature electronic coolers, *Prikl. Fiz.,* 1999, no. 3, pp. 123–125.
8. Tagiyev, M.M., Electrical anisotropy in extruded specimens of $Bi_{0.85}Sb_{0.15}$ solid solution, *Russ. Phys. J.,* 2018, vol. 60, no. 10, pp. 1795–1796. https://doi.org/10.1007/s11182-018-1283-z
9. Tagiyev, M.M., Effect of grain size and Pb doping on the thermoelectric properties of extruded samples of the $Bi_{0.85}Sb_{0.15}$ solid solution, *Inorg. Mater.,* 2021, vol. 57, no. 2, pp. 113–118.

10. Tagiyev, M.M., Dzhafarova, S.Z., Akhmedova, A.M., and Abdinova, G.D., Effect of grain size on the thermoelectric properties of the $Bi_2Te_{2.7}Se_{0.3}$ solid solution, *Izv. Vyssh. Uchebn. Zaved., Fiz.,* 2019, no. 3, pp. 104–109.
11. Sidorenko, N.A. and Dashevsky, Z.M., Effective Bi–Sb crystals for thermoelectric cooling at temperatures of $T \lesssim 180$ K, *Semiconductors,* 2019, vol. 53, no. 5, pp. 686–690. https://doi.org/10.1134/S1063782619050245
12. Zemskov, V.S., Belaya, A.D., Beluy, U.S., and Kozhemyakin, G.N., Investigation of thermoelectric properties of Bi–Sb alloy single crystals, *J. Cryst. Growth,* 2000, vol. 212, no. 1, pp. 161–166.
13. Ivanova, L.D., Petrova, L.I., Granatkina, Yu.V, Zemskov, V.S., Sokolov, O.B., Skipidarov, S.Ya., and Duvankov, V.I., Extruded materials for thermoelectric coolers, *Inorg. Mater.,* 2008, vol. 44, no. 7, pp. 687–691. https://doi.org/10.1134/S0020168508070030
14. Ivanova, L.D., Petrova, L.I., Granatkina, Yu.V., Zemskov, V.S., et al., Extruded Thermoelectric Materials Based on Bi_2Te_3–Bi_2Se_3 Solid Solutions, *Inorg. Mater.,* 2009, vol. 45, no. 2, pp. 148–153.
15. Ioffe, A.F., *Poluprovodnikovye termoelementy* (Semiconductor Thermoelements), Moscow: Nauka, 1960.
16. Ivanova, L.D., Thermoelectric materials for different temperature levels, *Semiconductors,* 2017, vol. 51, no. 7, pp. 909–912. https://doi.org/10.1134/S1063782617070132
17. Stepanov, N.P., Electron–plasmon interaction in bismuth with an acceptor dopant, *Russ. Phys. J.,* 2004, vol. 47, no. 3, pp. 262–271. https://doi.org/10.1023/B:RUPJ.0000038743.50158.a7
18. Markov, O.I., Graded band gap bismuth–antimony alloys, *Usp. Prikl. Fiz.,* 2014, vol. 2, no. 5, pp. 447–452.
19. Tagiyev, M.M. and Abdinova, G.D., Electrical and galvanomagnetic properties of extruded samples of $Bi_{85}Sb_{15}$ solid solutions with Pb and Te impurities, *Russ. Phys. J.,* 2019, vol. 61, no. 11, pp. 2135–2138.
20. Tagiyev, M.M. and Abdinov, D.Sh., Magnetothermoelectric Properties of Extruded Lead-Doped $Bi_{85}Sb_{15}$ Solid Solutions, *Inorg. Mater.,* 1995, vol. 31, no. 11, pp. 1274–1275.
21. Alieva, T.D. and Abdinov, D.Sh., Interfacial physicochemical and electrical effects in crystals of solid solutions in systems of contact materials, *Neorg. Mater.,* 1997, vol. 33, no. 4, pp. 27–38.
22. Okhotin, A.S., Pushkarskii, A.S., Borovikov, R.P., and Simonov, V.A., *Metody izmereniya kharakteristik termoelektricheskikh materialov i preobrazovatelei* (Characterization of Thermoelectric Materials and Converters), Moscow: Nauka, 1974.
23. Samedov, F.S., Tagiyev, M.M., and Abdinov, D.Sh., Effect of heat treatment on the properties of extruded Pb-doped $Bi_{0.85}Sb_{0.15}$ solid solutions, *Inorg. Mater.,* 1998, vol. 34, no. 7, pp. 704–706.
24. Oskotskii, V.S. and Smirnov, I.A., *Defekty v kristallakh i teploprovodnost'* (Structural Defects and Thermal Conductivity of Crystals), Leningrad, 1972.
25. Agaev, Z.F., Abdinova, G.D., Bagieva, G.Z., Tagiyev, M.M., and Abdinov, D.Sh., Thermal conductivity of extruded $Bi_{85}Sb_{15}$ doped with Gd and Pb, *Inorg. Mater.,* 2008, vol. 44, no. 2, pp. 130–132.
26. Gorelik, S.S. and Dashevskii, M.Ya., *Materialovedenie poluprovodnikov i dielektrikov* (Semiconductor and Dielectric Materials Research), Moscow: Metallurgiya, 1988.

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