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ELECTRICAL AND GALVANOMAGNETIC PROPERTIES OF EXTRUDED SAMPLES OF $Bi_{85}Sb_{15}$ SOLID SOLUTIONS WITH Pb AND Te IMPURITIES

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The effect of tellurium impurities on the electrical conductivity (σ), Seebeck coefficient (α), and Hall coefficient R of extruded $Bi_{85}Sb_{15}$ *+ 0.001 at.%* Pb *is studied in the temperature range 77–300 K. It is found that doping with tellurium impurities up to 0.001 at. % compensating acceptor* Pb *atoms leads to a strong decrease in the electron density and, consequently, to an increase in σ and significant decrease in the values of α and R. The materials obtained can be used as the n-branch of thermoelements operating at temperatures of ~77 K.*

Keywords: Seebeck coefficient, electrical conductivity, Hall coefficient, electrical properties, galvanomagnetic properties.

INTRODUCTION

Solid solutions of bismuth-antimony systems are promising materials for the creation of low-temperature electronic thermoelectric converters. In crystalline [1–5], extruded [6–9], and film [10, 11] samples of a Bi – Sb system, the highest values of the thermo- and magnetothermoelectric figure of merit Z_{MTE} are observed in the temperature range of 77–150 K at an antimony concentration of 9–15 at.%. By introducing either Te donor impurities or Pb or Sn acceptor impurities into these materials, it is possible to significantly change the electron concentration [12] and, as a result, the thermoelectric parameters — electrical conductivity (σ), thermo-e.m.f. (α), and thermal conductivity (χ). At the optimum value of the electron concentration, it is possible to optimize both the thermoelectric and magnetothermoelectric efficiency of solid solutions. A change in the concentration of charge carriers is accompanied by changes in their mobility and mean free path due to the scattering by phonons. This introduces additional changes in the properties of a thin film due to a change in the degree of manifestation of the classical size effect, which is associated both with the film thickness and with the size of crystallites in block films [12]. Searches for other active impurities (for example, Ag, In, and Au) did not give positive results due to their low solubility associated, in particular, with large difference between their atomic radii and atomic radii of Bi and Sb [13]. Optimization of thermoelectric parameters can be achieved by joint doping of solid solutions of Bi – Sb systems with acceptor and donor impurities. However, according to literary data, no such works have been carried out. Taking into account this fact, in the present paper, we investigate the effect of Te donor impurities on the electrical properties of extruded $Bi_{85}Sb_{15}$ samples containing lead acceptor impurities.

The experiments were carried out on the extruded samples of the $Bi_{85}Sb_{15}$ solid solution, since it was found that the extruded $Bi_{85}Sb_{15}$ samples had a thermoelectric figure of merit Z_{MTE} close to that of single-crystal samples, and their mechanical strength was significantly higher than that of single crystals [6–9]. During extrusion, a texture and

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TABLE 1. Dependence of Electrical Parameters of the Extruded $Bi_{85}Sb_{15}$+0.001 at.% Pb Samples on the Tellurium Concentration at 77 K

$Bi_{85}Sb_{15}$ + 0.001 at.% Pb + Te_x				$Bi_{85}Sb_{15}$ + Te_x		
Te content, at.%	σ, $Ohm^{-1}\cdot cm^{-1}$	α, μV/K	R, cm^3/C	σ, $Ohm^{-1}\cdot cm^{-1}$	α, μV/K	R, cm^3/C
0	1462	–90	–5.0	5250	–182	–26.5
0.0001	2021	–172	–11.11	7574	–151	–14.5
0.0005	1604	–155	–10.63	7640	–161	–23.9
0.001	1502	–179	–12.52	18406	–57	–3.3
0.005	13752	–31	–0.72	20585	–36	–1.6
0.01	17027	–57	–0.69	22534	23	0.9
0.05	17941	–9	–0.96	24510	12	–0.3
0.1	15600	–4	0.0	24753	–7	–0.3

deformation structural defects appear in the material [14]. By selecting the mode of post-extrusion heat treatment, optimization of these factors affecting the thermoelectric parameters of the alloy can be achieved [15].

1. EXPERIMENTAL PART

The extruded samples of $Bi_{85}Sb_{15}$ with lead and tellurium impurities were obtained according to the technology described in [16]. The Pb and Te dopants were introduced during the synthesis. Samples in the form of rectangular parallelepipeds 3×5×11 mm in size were cut from the extruded rods on an electrical erosion setup. Removal of the damaged layer formed on the surface of the samples during cutting was carried out by electrochemical etching. The samples were annealed in quartz ampoules evacuated to a pressure of 10^{-1} Pa at a temperature of ~503 K for 2 h.

The electrical parameters were measured along the extrusion axis (along the rod) in the temperature range 77–300 K by the DC probe method. The measurements were carried out on samples that did not undergo annealing after extrusion and on the same samples that underwent annealing.

2. RESULTS AND DISCUSSION

The measurement results are presented in Table 1 and in Fig. 1. It can be seen that the signs of the thermo-e.m.f. coefficient α and Hall coefficient R of the sample containing 0.001 at.% Pb are negative, but the values of α and R are significantly lower than those of the $Bi_{85}Sb_{15}$ sample not doped with Pb. The temperature dependences of α and R for this sample is of the semiconductor type, as in case of the $Bi_{85}Sb_{15}$ sample not doped with lead.

The semiconductor character of the dependences σ(T) and R(T) is also possessed by samples containing 0.0001–0.001 at.% Te. However, in these samples, the absolute values of α and R are 2–2.5 times higher than those in the sample not doped with tellurium. A further increase in the tellurium concentration in the $Bi_{85}Sb_{15}$ + 0.001 at.% Pb sample is accompanied by a stronger (by 10 times) increase in σ and a decrease in the values of α and R. The type of conductivity is electronic in all cases. The samples containing 0.005–0.1 at.% Te have a metallic character of the dependence σ(T), which is well correlated with the dependences α(T) and R(T) in these samples.

The $Bi_{1-x}Sb_x$ alloys represent a continuous series of solid substitution solutions. The entire concentration range of $Bi_{1-x}Sb_x$ alloys is divided into three characteristic regions: a semi-metallic region ($0 \le x \le 0.065$), a semiconductor region ($0.065 < x < 0.23$), and a semi-metallic one ($0.23 < x < 1$) [17]. Electrical properties of the $Bi_{85}Sb_{15}$ alloys are in good agreement with these data.

The lead atoms create acceptor levels in the $Bi_{85}Sb_{15}$ solid solution and, compensating electrons, reduce σ from about 5250 $Ohm^{-1}\cdot cm^{-1}$ for an undoped sample to about 1500 $Ohm^{-1}\cdot cm^{-1}$ for a sample with 0.001 at% Pb. The data on the influence of the magnetic field on σ of the $Bi_{85}Sb_{15}$ samples with 0.001 at.% Pb [18] show that both electrons and holes are involved in conduction, i.e., electrons are not fully compensated by the acceptor lead atoms. When doping of

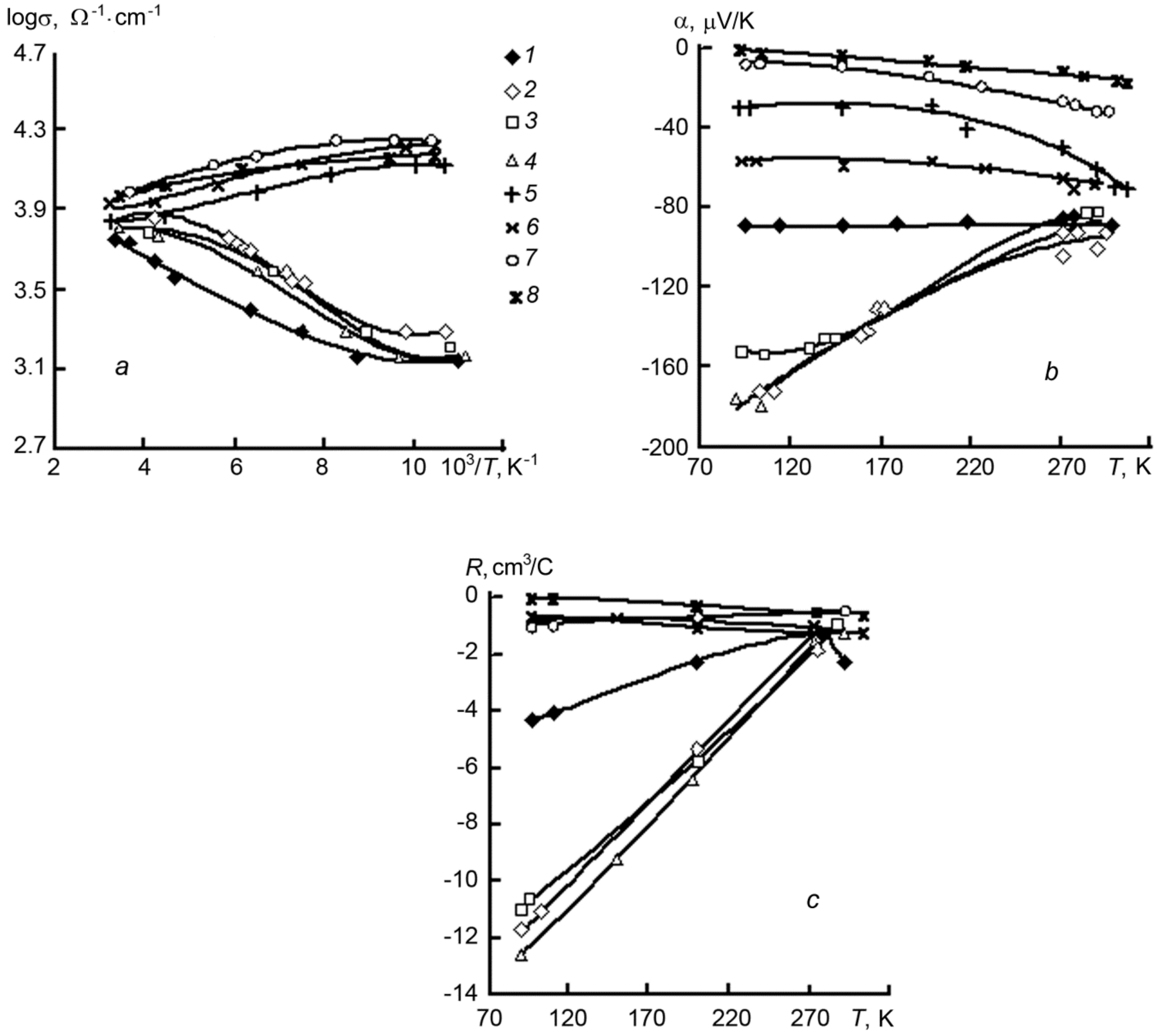

Fig. 1. Temperature dependences of the electrical conductivity σ (*a*), thermo-e.m.f. coefficient α (*b*), and Hall coefficient *R* (*c*) of $Bi_{85}Sb_{15}$+0.001 at.% Pb samples with tellurium impurity: curves *1–8* refer to the samples with 0, 0.0001, 0.0005, 0.001, 0.005, 0.01, 0.05, and 0.1 at.% Te, respectively.

the extruded $Bi_{85}Sb_{15}$ + 0.001 at.% Pb samples with donor tellurium atoms, initially (up to 0.001 at.% Te), compensation of acceptor Pb atoms and then, an increase in the electron concentration occur, i.e. an increase in σ and a decrease in the absolute values of α and *R* take place. In this case, the character of the dependences σ(*T*) and *R*(*T*) becomes metallic. The power parameters ($\alpha^2\sigma$) for the samples with 0.0001–0.001 at.% Te are within (48.1–59.8)$\cdot 10^{-6}$ W/(cm·K^2).

For comparison, Table 2 shows the data on the effect of tellurium impurities on the electrical properties of a pure (free of lead atoms) extruded $Bi_{85}Sb_{15}$ sample.

It can be seen from the data of Tables 1 and 2 that the compensating actions of lead impurities occur at all tellurium contents.

TABLE 2. Dependences of electrical parameters of extruded $Bi_{85}Sb_{15}$ samples on the concentration of Te at ~77 K

Te content, at.%	σ, $Ohm^{-1} \cdot cm^{-1}$	α, μV/K	R, cm^3/C
0	5270	–182	–26.5
0.0001	7574	–151	–14.5
0.0005	7640	–161	–23.9
0.001	18604	–57	–3.3
0.01	20585	–36	–1.6
0.05	24510	–12	–0.3
0.1	24753	–7	–0.3

CONCLUSIONS

It is found that doping of the extruded $Bi_{85}Sb_{15}$ samples containing 0.001 at.% of acceptor lead impurities with tellurium donor impurities allows obtaining samples with the thermo-e.m.f. coefficient close to the thermo-e.m.f. coefficient of a pure $Bi_{85}Sb_{15}$ sample, an electrical conductivity of ~1500 $Ohm^{-1} \cdot cm^{-1}$, and a power parameter within $(48.1–59.8) \cdot 10^{-6}$ $W/(cm \cdot K^2)$ at 77 K, which can be recommended as the n-branch of thermoelements operating at temperatures of ~77 K.

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