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Structural Defects and Electrical Properties of Extruded Samples of $Bi_{85}Sb_{15}$ Solid Solutions

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Abstract

The effect of 5 hours annealing in vacuum $\sim 10^{-3}Pa$ at $503K$ on the electroconductivity (σ), the coefficient of thermoelectric power (α) and the Hall coefficient (R_x) for extruded samples of $Bi_{85}Sb_{15}$ has been investigated in the temperature range from $\sim 77K$ up to $\sim 300K$. The samples were taken with a different concentration of Pb (lead) up to $\sim 0.1a.w\%$. The anisotropy of electrical properties of these samples was also studied in the temperature range between $77K$ and $300K$ and in the presence of magnetic field up to $\sim 74 \times 10^4 A/m$. It is established that unannealed samples are nearly insensitive to the amount of lead and to the strength of the applied magnetic field. With increasing the amount of Pb we observed inversion of signs of α and R_x from n to p-type. The obtained results are interpreted within the assumption that the extrusion of $Bi_{85}Sb_{15}$ samples may give rise to a creation of deformation defects which act as scattering centers for electrons and disappear with annealing.

Extruded samples of $Bi_{85}Sb_{15}$ solid solutions have magnetothermoelectric properties which are similar to those of single crystals with the same content [1-3]. However their mechanical properties are considerably higher than those of single crystals. The latter peculiarities make the extruded samples more perspective for developing of low-temperature energy transformers.

In the present paper the effect of annealing on the electroconductivity, the coefficient of thermoelectric power as well as the Hall coefficient are experimentally investigated for extruded samples of $Bi_{85}Sb_{15}$ with various impurity concentrations of Pb. The extruded samples of $Bi_{85}Sb_{15}$ were obtained by the method described in [2]. Two types of the samples were investigated; the first ones were cut immediately after extrusion, while as the later samples were annealed in vacuum $\sim 10^{-3}Pa$ at $503K$ for 5 hours. It is known [3] that the thermoelectric parameters of these solutions are completely stabilized after annealing at $503K$ during 5 hours. The obtained results are presented in Figures 1-4 and in Table 1. It is seen that for both annealed and unannealed samples the dependences of σ, α, R_x on the impurity concentration of Pb are almost identical, however annealed samples are more sensitive to the Pb content and to the strength of magnetic field. We observe the following peculiarities at $77K$; undoped samples and samples with concentrations of Pb up to $0.01 a.w.\%$ have n-type conductivity, whereas samples with the concentration $0.05 a.w.\%$ and higher exhibit p-type conductivity.

In all cases at $77K$ and in the absence of magnetic field, annealing increases the electroconductivity and the Hall coefficient. At the same time the thermoelectric power of undoped samples and samples with $0.001 a.w.\%$ of Pb (i.e. samples with high electron conductivity) are not essentially changed with annealing. However, with increasing of Pb content up to $0.01 a.w.\%$, the effect of annealing on the electroconductivity is considerably diminished and with 0.01 and $0.05 a.w.\%$ impurity concentrations the annealing barely influences the electroconductivity. Annealing of samples with $0.01 a.w.\% Pb$ results in an α and R_x increase of approximately 2 times, while the electroconductivity remains electron-type.

The influence of magnetic field on the σ of samples having n-type conductivity are more stronger than that for samples with p-type conductivity. The magnetoresistivity of annealed samples with n-type conductivity is always greater (~ 3 times) than that of unannealed ones; while for p-type samples (samples with the concentration $0.01 a.w.\%$ and higher) the magnetoresistivity almost does not depend on annealing.

Undoped samples and samples with $0.01 a.w.\% Pb$ in all the studied ranges of the magnetic field exhibit n-type conductivity, whereas samples with $0.05 a.w.\% Pb$ have p-type conductivity. Samples with concentrations 0.005 and 0.01 at $\% Pb$ change the type of conductivity with increasing of the applied magnetic field. In both cases, inversion of signs of the conductivity for annealed samples occurs at values of the magnetic field which are approximately 2-2.5 times less than those for unannealed samples.

With increasing temperature the influence of the magnetic field as well as Pb impurities on the electrical properties of pure alloys up to the concentration $0.01 a.w.\%$ of Pb become weak. At temperatures higher than $130 - 140K$ all the samples doped with Pb are n-type. In samples with p-type conductivity in the temperature range from $77K$ up to the temperature, at which the inversion of signs of the conductivity occurs, the magnetoresistivity increases, however higher this temperature range the latter decreases, remaining at $300K$ greater than at $77K$.

It is known that due to deformations arising under extrusion of $Bi_{85}Sb_{15}$ solid solutions texture and defects of lattice are created. Structural changes caused by the deformations may give rise to a sharp change of the structural, mechanical and electrical properties [4]. The creation of defects results in more effective scattering of electrons and holes and decreases their mobility. The concentration of free carriers also increases due to the creation of electrically active centers on these defects. Annealing at $503K$ decreases the amount of structural defects, i.e. increases the mobility and decreases the concentration of the carriers. Therefore the electroconductivity σ and the Hall coefficient R_x of undoped samples of $Bi_{85}Sb_{15}$ are increased after annealing (~ 3 and ~ 2 times respectively). On the other hand, a negligible change of the coefficient of thermoelectric power α under annealing serves, apparently, in favour of the fact that a change of the Hall coefficient R_x after annealing may be mainly caused by a change of parameters characterizing a scattering mechanism in material. From here it also follows that the defects appearing in $Bi_{85}Sb_{15}$ after extrusion are mainly not electroactive.

Table 1. Electrical parameters of extruded samples of $Bi_{85}Sb_{15}$ solid solutions at $\sim 77K$.

Cont.	Parameters of non-annealed patterns. Intensity of the magnetic field: $H = 0$		$H = 7.5 \times 10^4 A/m$		$H = 74 \times 10^4 A/m$	
$Pb, a.w.\%$	$\sigma, Ohm^{-1}cm^{-1}$	$\alpha \times 10^6, V/K$	$R_x, cm^3/Cl$	$\sigma, Ohm^{-1}cm^{-1}$	$\alpha \times 10^6, V/K$	$R_x, cm^3/Cl$
0	5287	-178	-19.72	602	-235	-27.09
0.001	2446	-188	-24.05	333	-200	-28.06
0.005	978	-121	+1.12	305	+195	+6.91
0.01	885	-144	+1.11	309	+199	+3.11
0.05	1442	+83	+1.11	1460	+125	+1.17
0.075	2030	+74	+1.11	1832	+102	+0.75
0.1	2402	+63	+0.83	2168	+84	+0.78

Cont.	Parameters of annealed patterns. Intensity of the magnetic field: $H = 0$		$H = 7.5 \times 10^4 A/m$		$H = 74 \times 10^4 A/m$	
$Pb, a.w.\%$	$\sigma, Ohm^{-1}cm^{-1}$	$\alpha \times 10^6, V/K$	$R_x, cm^3/Cl$	$\sigma, Ohm^{-1}cm^{-1}$	$\alpha \times 10^6, V/K$	$R_x, cm^3/Cl$
0	1754	-185	-9.44	618	-190	-12.5
0.001	1229	-176	-10.55	502	-159	-9.97
0.005	702	-72	-0.48	364	+24	+0.56
0.01	884	-78	-0.27	443	+26	+0.36
0.05	1734	+67	+1.11	1459	+100	+1.03
0.075	1791	+53	+0.55	1527	+89	+0.81
0.1	1984	+48	+0.27	1777	+67	+0.61

Table 2. Parameters of extruded samples of $Bi_{85}Sb_{15}$ solid solutions in the directions along and perpendicular to the axis of extrusion.

Directions at which the measurements of paremeters were carried out	Parameters of non annealed patterns: $\sigma, Ohm^{-1}cm^{-1}$		$\alpha \times 10^6, V/K$		$R_x, cm^3/Cl$	
	77 K	300 K	77 K	300 K	77 K	300 K
Along the axis of extrusion	1761	6455	172	94	9.44	0.97
Perpendicular to the axis of extrusion	1989	7053	177	98	7.74	0.76

Directions at which the measurements of paremeters were carried out	Parameters of non annealed patterns: $\sigma, Ohm^{-1}cm^{-1}$		$\alpha \times 10^6, V/K$		$R_x, cm^3/Cl$	
	77 K	300 K	77 K	300 K	77 K	300 K
Along the axis of extrusion	5230	7520	181	95	26.5	1.43
Perpendicular to the axis of extrusion	4308	5820	169	87	21.7	20.75

With increasing the Pb content the effect of annealing on σ decreases and in the case of samples with 0.01, $0.05a.w.\%$ of Pb annealing almost does not influence on σ. This shows that the deformation defects in $Bi_{85}Sb_{15}$ mainly scatters electrons, while holes are almost not scattered by these defects. With increasing temperature the electron conductivity becomes predominant and, therefore, at temperatures higher than the inversion temperature for signs of α and R_x, the magnetoresistance of samples increases.

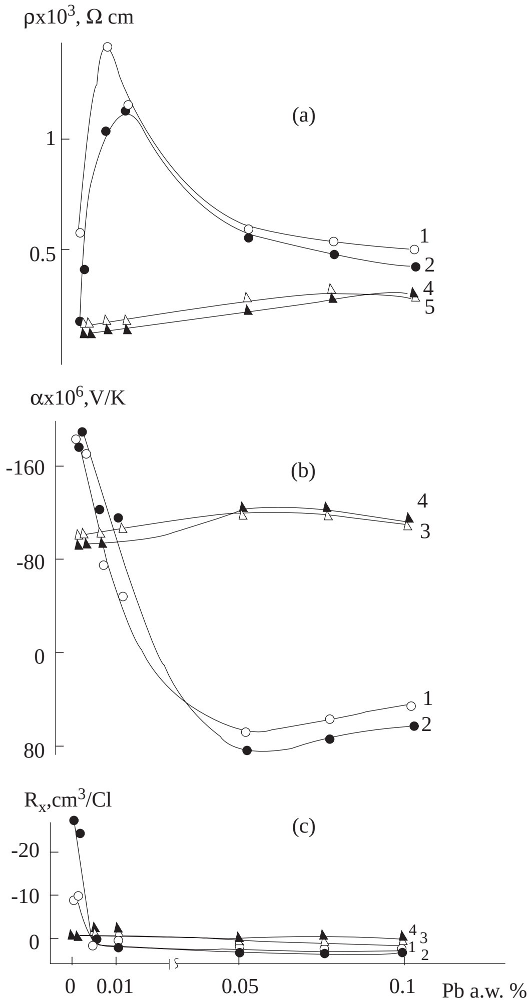

Figure 1. Dependences of the electroresistivity (a), thermoelectric power (b) and the Hall coefficient (c) of extruded samples of $Bi_{85}Sb_{15}$ on the concentration of Pb at $\sim 77K(1,2)$ and at $\sim 300K$ (3, 4). The curves 1 and 3 correspond to non-annealed samples, while 2 and 4 refer to annealed samples.

Annealing also influences on the anisotropy of electrical properties of the extruded samples. These results are shown in Table 2. The optimal direction of growth of $Bi_{1-x}Sb_x$ single crystals is the crystallographic direction (110) of the rhombohedral cell. However the highest values of the thermoelectric efficiency as well as the electroconductivity are attained in the other direction (111), which is perpendicular to the direction of optimal growth. Apart from this in the single crystals more pronounced plane of connection is

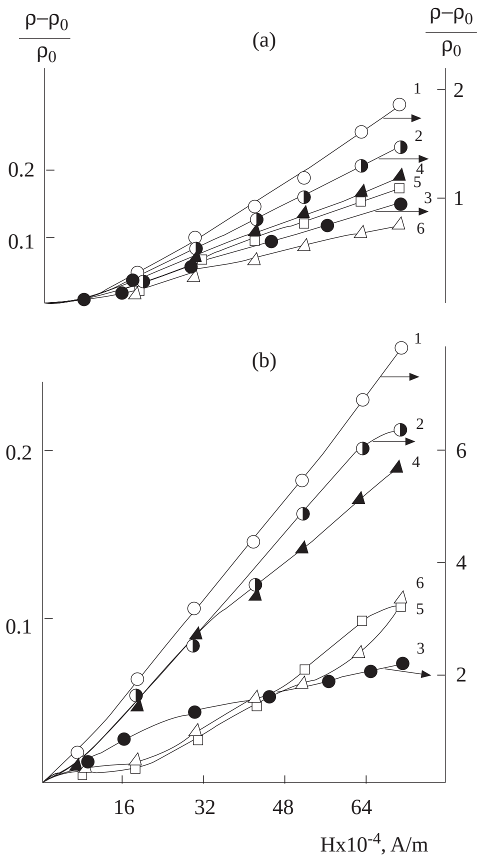

Figure 2. Dependences of the magnetoresistivity on the magnetic field at $\sim 77K$ for unannealed (a) and annealed (b) samples. The curves correspond to undoped sample (1) and to the samples doped by 0.001 (2), 0.005 (3), 0.05 (4), 0.075 (5) and 0.1 a.w. % Pb (6).

the (111) plane, along which they can be cleaved [4,5]. In the Bi crystals and alloys of $Bi - Sb$ the anisotropy of electrical parameters is caused by the anisotropy of the Fermi levels, i.e. maxima which take place in the conductivity, and also by the differences in scattering of carries in different directions.

One may suppose that under extrusion of the polycrystalline $Bi_{85}Sb_{15}$ material an axial texture arises [6], i.e. a part of particles of polycrystalline material is oriented so that their trigonal axis becomes parallel to the extrusion axis. At the same time, as a result of plastic deformations, different defects are created in different particles and these structural defects are predominantly collected between (111) planes.

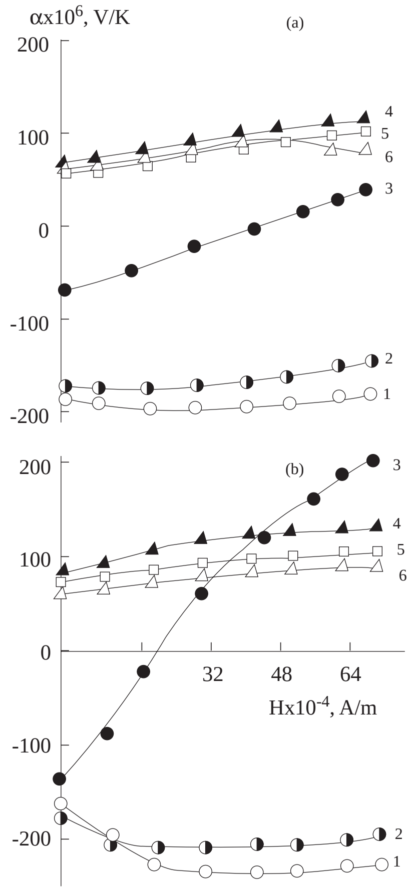

Figure 3. Dependence of the coefficient of thermoelectric power on the magnetic field at $\sim 77K$ (notations are the same as in Fig. 2).

Therefore in extruded samples, which are not annealed, electrons are more strongly scattered along the extrusion axis than in the direction perpendicular to the latter.

Isothermic annealing gives rise to a decrease of concentrations of structural irregularities. As a result of this the concentration of free carriers decreases, while their mobility increases, which, in turn, is reflected on the changes of values of the quantities σ, α and R_x. Note that more pronounced changes take place at low temperatures $\sim 77K$, where a role of the impurity conductivity and the scattering of electrons on the defects are predominant. At $\sim 300K$ the predominant scattering mechanism is a scattering on the acoustical phonons. Therefore at $77K$ the anisotrophy of electroconductivity σ for annealed samples is opposite to that for unannealed samples.

Our X-ray measurements confirmed the appearance of a texture under extrusion of $Bi_{85}Sb_{15}$ alloys and also showed that annealing does not give rise to a texture of recrystallization in the samples of $Bi_{85}Sb_{15}$. However annealing at $503K$ results in a partial destruction of the texture. Apparently, it may be regarded as a reason for the fact that at the temperature $\sim 300K$ and in the direction perpendicular to the axis of extrusion the electroconductivity of samples with annealing decreases from the values $\sim 7053 Ohm^{-1}cm^{-1}$ to $\sim 5820 Ohm^{-1}cm^{-1}$.

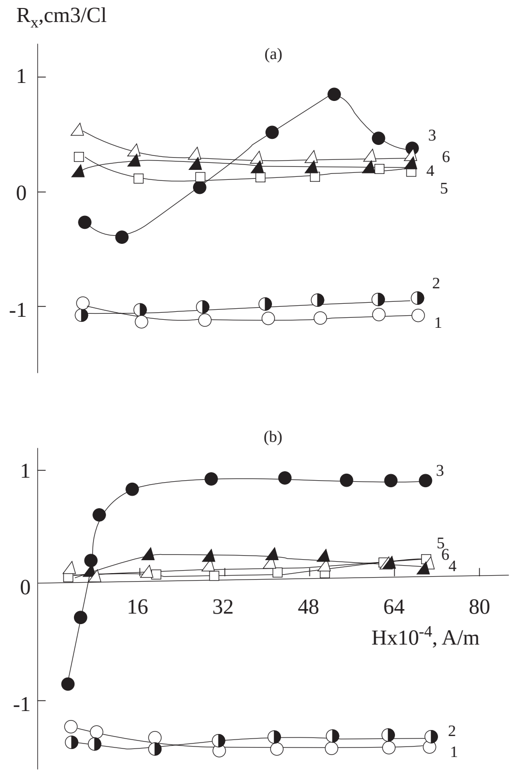

Figure 4. Dependence of the Hall coefficient on the magnetic field at $\sim 77K$ (notations are the same as in Figure 2).

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