MAGNETOELECTRIC PROPERTIES OF ANISOTROPIC THERMOELECTRICS BASED ON EXTRUDED SAMPLES OF SOLID SOLUTION $Bi_{0.85}Sb_{0.15}$ DOPED WITH TELLURIUM

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The influence of tellurium impurities and heat treatment on the anisotropy of the magnetoelectric properties of extruded samples of the $Bi_{0.85}Sb_{0.15}$ solid solution in the range of ~77−300K and magnetic field strengths up to ~74x10^4 A/m was studied. It was found that in annealed samples of $Bi_{0.85}Sb_{0.15}$ with 0.001 at.% tellurium, the absolute values of α in the direction perpendicular to the extrusion axis are more sensitive to the magnetic field than in the parallel direction and the anisotropy of the thermopower (Δα) at a magnetic field strength H = 42x10^{4}A/ m reaches the value Δα =80 μV/K at ~77K.

Key words: extrusion, anisotropy, annealing, impurity, electrical conductivity.
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INTRODUCTION

Recently, interest in anisotropic thermoelements have increased significantly, due to the maximum values of thermoelectric efficiency (Z) possessed in anisotropic substances. Extruded samples of solid solutions of Bi-Sb systems are the most effective material for creating various thermo- and magnetothermoelectric energy converters [1-3]. In connection with the anisotropy of the electrical and thermal properties of solid solutions of Bi-Sb systems, it is of interest to identify interplanar spaces (layers) with maximum and minimum values of electrical conductivity σ thermopower coefficients α and thermal conductivity χ, which allows these parameters to vary depending on temperature and magnetic field intensity (H) .

Doping with different types of solid solution impurities of Bi-Sb systems can optimize the concentrations of charge carriers, which are the main charge carriers in this material. Bismuth and bismuth-antimony alloys have a layered structure, so charge carriers are scattered differently in different directions, which leads to anisotropy of electrical and thermal parameters. Therefore, the study of the anisotropy of the electrical properties of solid solutions of Bi-Sb systems depending on the nature and concentration of magnetic field impurities, heat treatment in a wide temperature range to create more efficient anisotropic thermoelements, which lead to widespread practical applications of these materials and devices based on them, is relevant. The effect on the anisotropy of the electrical and thermal properties of extruded samples of the $Bi_{0,85}Sb_{0,15}$ solid solution of acceptor-type impurities in various concentrations of lead and donor-type tellurium in concentrations of 0.0005 at% was studied in [4]. The effect of tellurium impurities in various concentrations on the anisotropy of the magnetoelectric properties of extruded samples of $Bi_{0,85}Sb_{0,15}$ solid solutions has not been studied.

Taking into account the above, in this work, in order to clarify the influence of tellurium impurities in various concentrations, heat treatment and magnetic field on the anisotropy of the electrical properties of extruded samples of the $Bi_{0,85}Sb_{0,15}$ <Te_x> solid solution, its extruded samples were obtained and their electrical conductivity (σ), coefficients thermopower (α) and Hall power (R_H) in the range of ~77−300K and magnetic field strength up to ~74x10^4 A/m in parallel and perpendicular directions to the extrusion axis.

EXPERIMENTAL PART

The technology sequence for obtaining extruded samples of $Bi_{0,85}Sb_{0,15}$<Te_x> ((0,0001<x<0,1) at.%) solid solutions is shown in [3].

Electrical parameters were measured along and perpendicular to the direction of the extrusion axis.

We studied samples that had not undergone heat treatment after extrusion and the same samples that had undergone annealing. The results obtained are presented in the table. The table shows the absolute values of the thermopower (α) and Hall coefficients (R_H).

RESULTS AND DISCUSSIONS

With increasing tellurium concentration, the electrical conductivity of all samples increases, relative to the undoped $Bi_{0,85}Sb_{0,15}$ sample, in both directions of the extrusion axis. A particularly strong change occurs at low temperatures, where impurity conductivity

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prevails. A similar influence of tellurium is observed on the coefficients α and R_H. In samples with low tellurium concentrations and those that have undergone annealing, the electrical parameters are more sensitive to tellurium concentrations than samples that have not been annealed in parallel and perpendicular directions to the extrusion axis. As the tellurium concentration increases, the effects of annealing and magnetic field on the electrical properties are weakened. In samples with tellurium concentrations of 0.05 at.% Te and more, untreated and subjected to heat treatment, the influence of the magnetic field on the electrical properties is almost absent.

It can be seen that during heat treatment in $Bi_{0,85}Sb_{0,15}$<0,001Te> samples there is a significant change in the absolute values of thermopower, with a simultaneous slight increase in electrical conductivity and Hall coefficient in parallel and perpendicular directions to the extrusion axis.

In samples with 0.1 at.% tellurium, the effect of heat treatment on the electrical properties is greatly weakened.

Heat treatment leads to a decrease in the concentration of structural defects in the studied samples that arise during previous technological operations (during plastic deformation), to an increase in mobility μ and an increase in the prevalence of current carrier scattering.

In extruded samples, there are defects that are difficult to anneal, causing changes in the concentration of current carriers and their mobility μ. Such defects can be twin boundaries or stacking faults that arise during plastic deformation. When obtaining $Bi_{0,85}Sb_{0,15}$ samples, an axial texture is formed due to plastic deformation, i.e. the trigonal axis of part of the polycrystalline grains is oriented in a parallel direction to the extrusion axis.

With optimal heat treatment of the studied samples, the concentration of structural defects decreases, which leads to an increase in the mobility of current carriers, which is reflected in changes in the values of the coefficients σ, α and R_H.

In samples of the $Bi_{0,85}Sb_{0,15}$ solid solution doped with tellurium in a small amount (up to ~0.0005 at.% Te) with increasing magnetic field, the magnetoresistance increases and the value $\sigma_{||}>\sigma_{\perp}$. In all cases, in a magnetic field $\sigma_{||}>\sigma_{\perp}$. At high tellurium concentrations, the anisotropy σ and its dependence on the magnetic field are further weakened.

When doping extruded $Bi_{0,85}Sb_{0,15}$ samples with up to 0.1 at.% tellurium that have not undergone heat treatment, in the samples in the absence of a magnetic field over the entire temperature range, the conductivity in the perpendicular direction of extrusion $\sigma_{\perp}$ is higher than in the parallel direction of the extrusion axis $\sigma_{|}$. After annealing, this ratio changes to the opposite, i.e. the anisotropy of electrical conductivity in undoped samples and samples with low tellurium concentrations changes its sign.

The coefficients α and R_H of samples doped with tellurium also exhibit anisotropy. At ~77K in undoped samples and samples doped with 0.001 at.% tellurium and subjected to heat treatment, the anisotropy of α and R_H increases with increasing magnetic field strength. The experimental data obtained in samples doped with tellurium are satisfactorily explained by a change in the crystal structure of $Bi_{0,85}Sb_{0,15}$.

During heat treatment, deformation defects formed during plastic deformation, which are centers for electrons, are “healed” [5]. As a result, σ of undoped $Bi_{0,85}Sb_{0,15}$ samples and samples doped with tellurium at ~77K increases strongly in the direction of the extrusion axis, and anisotropy σ changes its sign.

The magnetic field increases the resistivity of doped and undoped solid solution samples of $Bi_{0,85}Sb_{0,15}$ samples. It affects samples unalloyed and doped with 0.0005 at.% Te more strongly, and to a lesser extent at higher tellurium concentrations 0.1 at.% Te. The absolute values of magnetic resistivities decrease with increasing temperature, due to increased scattering of charge carriers. The influence of the magnetic field on σ of samples doped with 0.0005 at.% Te and undergone heat treatment is greater than in samples that have not undergone heat treatment. At tellurium concentrations of 0.1 at%, the effect of heat treatment and magnetic field on σ is almost absent (insignificant).

At high temperatures (~300K), samples of the $Bi_{0,85}Sb_{0,15}$ solid solution are an intrinsic semiconductor; electrons are mainly scattered by acoustic vibrations of the lattice. Therefore, at high temperatures, the effects of heat treatment, tellurium impurities and magnetic field do not have a noticeable effect on ρ of the samples. The change in ρ at high temperatures, at high tellurium concentrations (up to ~0.1 at.% Te) is probably due to a change in the band gap in the studied samples. However, the anisotropy of electrical properties relative to the extrusion axis remains at ~300K. Tellurium in an amount of 0.0001 at.% practically does not change the value of α. A further increase in its concentration leads to a decrease in the absolute value of α, especially at low temperatures. In $Bi_{0,85}Sb_{0,15}$<Te> alloys heavily alloyed with tellurium, the thermopower becomes anisotropic.

Anisotropy α can be associated with the presence of several nonequivalent extrema in the conduction band or several scattering mechanisms with different anisotropy of the relaxation time.

Small absolute value of α with strong degeneracy, i.e. at high tellurium concentrations, it provides only a non-parabolic zone if scattering occurs on acoustic phonons.

In samples containing up to 0.0005 at.% Te, heat treatment has little effect on the absolute value of α in the absence of H. In unannealed and annealed samples unalloyed and doped with tellurium up to 0.005 at.%, a significant change in α under the influence of a magnetic field is observed at low temperatures. In $Bi_{0,85}Sb_{0,15}$ samples with a tellurium concentration of 0.001 at.% that underwent heat treatment, the absolute value of α in the perpendicular direction is more sensitive to the magnetic field than in the parallel direction to the extrusion axis. In the same samples, the thermopower anisotropy value (Δα) at magnetic field strength $H = 42x10^4$ A/m is $\Delta\alpha = 77$ μV/K

Table 1.

Electrical parameters of extruded samples of $Bi_{0,85}Sb_{0,15}$ ‹Te› solid solution in parallel and perpendicular directions relative to the extrusion axis

Sample		77K																	
		H=0								H=42×10⁴ A/m				H=74×10⁴ A/m					
		before heat treatment				after heat treatment				before heat treatment		after heat treatment		before heat treatment		after heat treatment			
		σ Ω⁻¹/cm⁻¹	α, μV/K	R_H × 10⁻⁸ cm³/C	μ,cm²/(V s)	σ Ω⁻¹/cm⁻¹	α, μV/K	R_H × 10⁻⁸ cm³/C	μ,cm²/(V s)	σ Ω⁻¹/cm⁻¹	α, μV/K	σ Ω⁻¹/cm⁻¹	α, μV/K	σ Ω⁻¹/cm⁻¹	α, μV/K	σ Ω⁻¹/cm⁻¹	α, μV/K		
Parallel to the direction	$Bi_{0,85}Sb_{0,15}$	2414	172	14.32	34569	5230	181	26.5	38595	1493	219	2521	212	932	240	1856	273		
	$Bi_{0,85}Sb_{0,15}$+0,0001at.%Te	3025	177	13,59	41109	7574	151	23,65	79125	1470	185	4000	207	1215	191	2342	244		
	$Bi_{0,85}Sb_{0,15}$+0,0005at.%Te	5910	161	11,4	67374	7695	161	23.97	84449	2634	198	3875	238	1930	248	1799	264		
	$Bi_{0,85}Sb_{0,15}$+0,001 at.%Te	7354	109	4.67	34343	6360	118	9,71	61756	4831	114	5972	121	4520	116	5391	133		
	$Bi_{0,85}Sb_{0,15}$+0,005 at.%Te	8210	103	8,93	73315	9861	113	5,1	50291	8971	105	9121	116	8782	106	8791	124		
	$Bi_{0,85}Sb_{0,15}$+0,1at.%Te	19585	11	0.15	2937	20071	9	0.14	2810	17953	11	186	12	7234	12	2077	13		
In the perpendicular direction	$Bi_{0,85}Sb_{0,15}$	2735	177	11.78	32218	4308	169	21.72	93570	1581	221	2114	222	1051	235	1134	271		
	$Bi_{0,85}Sb_{0,15}$+0,0001at.%Te	4231	174	14,2	60080	7121	149	19,8	140996	1735	178	3472	214	1412	189	1986	240		
	$Bi_{0,85}Sb_{0,15}$+0,0005at.%Te	8921	160	4.67	41661	6785	160	20.89	41739	2931	191	3131	231	2113	240	1432	261		
	$Bi_{0,85}Sb_{0,15}$+0,001 at.%Te	7421	102	4.25	31539	5158	87	7,8	40232	5022	112	5232	201	4875	112	4621	210		
	$Bi_{0,85}Sb_{0,15}$+0,005 at.%Te	9471	73	4,25	13165	9475	111	4,7	44533	9021	70	8824	113	8921	103	7210	119		
	$Bi_{0,85}Sb_{0,15}$+0,1at.%Te	22057	12	0.25	5514	18519	7	0.03	556	21930	12	978	12	21790	13	19689	13		

At high tellurium concentrations, R_H of the samples is almost independent of temperature. This behavior of R_H confirms the presence of a large electronic contribution to the transfer phenomenon in $Bi_{0,85}Sb_{0,15}$ <Te> samples.

Bismuth-antimony alloys have a layered structure, so charge carriers are scattered differently in different directions. Due to the fact that charge carriers are scattered more strongly along cleavage planes, the anisotropy ρ changes with temperature. With increasing temperature, the carrier relaxation time decreases faster in the direction of the trigonal axis. With increasing temperature, the mean free path of charges decreases, and the influence of the anisotropy of Fermi surfaces on the anisotropy ρ of bismuth and Bi-Sb alloys at high temperatures is weakened.

Thus, the anisotropy of the electrical properties of extruded $Bi_{0,85}Sb_{0,15}$ samples is caused by texture formation along the extrusion axis during plastic deformation. In this case, the anisotropy coefficient depends on the tellurium concentration and heat treatment, which is mainly due to the change in the contribution to the conductivity of various charge carriers from the corresponding Fermi extrema.

CONCLUSION

It was found that unannealed samples of the $Bi_{0,85}Sb_{0,15}$ solid solution are more sensitive to Te impurities at low concentrations than samples that have undergone heat treatment. As the tellurium concentration increases, the influence of tellurium impurities and the magnetic field on the resistivity of samples that have undergone and have not undergone heat treatment is weakened. Due to the fact that bismuth-antimony crystals have a layered structure, the defects formed in them during plastic deformation are concentrated predominantly between the (111) planes. As a result, in extruded samples doped with tellurium and subjected to heat treatment, electrons are scattered more in the perpendicular direction of the extrusion than in the direction of the extrusion axis. The increase in mobility and electrical conductivity in the direction parallel to the extrusion axis as a result of heat treatment is greater than in the direction perpendicular to the extrusion axis. In this regard, in samples that have undergone annealing, the anisotropy σ at ~77 K is opposite to that of samples that have not undergone annealing.

In extruded samples of $Bi_{0,85}Sb_{0,15}$ with 0.001 at.% Te that underwent heat treatment, the absolute values of α in the direction perpendicular to the extrusion axis are more sensitive to the magnetic field than in the parallel direction. In these samples, the thermopower anisotropy value (Δα) at a magnetic field strength H = 42x10^4 A/m reaches the value Δα = 80 μV/K. High mechanical strength properties and values of Δα =80 μV/K allow us to recommend this material for the creation of highly efficient anisotropic thermoelements.

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