ELECTRICAL AND THERMAL PROPERTIES OF THE SOLID SOLUTIONS OF Bi-Sb SYSTEMS WITH VARIOUS IMPURITIES

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Investigated the electrical conductivity (σ), the coefficients of thermal emf (α), Hall (R_x) and thermal conductivity (χ) extruded samples $Bi_{0.85}Sb_{0.15}$ with different impurities in the temperature range *77-300K*, and the magnetic field strength of ~1.0 Tesla after extrusion and these same samples, the last joke. It is shown that the conductivity type of extruded samples $Bi_{0.85}Sb_{0.15}$ *at* low temperatures can be controlled by introducing impurities of Pb and applying a magnetic field.

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1. Introduction

Solid solutions of Bi-Sb have a record high thermoelectric efficiency *Z* at low temperatures. A material based on solid solutions of Bi-Sb system is used to create the low-temperature heat and magnetothermoelectric and photovoltaic cells, and are promising materials in this direction. However, due to the structure of monocrystals laminate Bi-Sb systems, have low mechanical strength, which limits their application in the construction of low-temperature electronic converters. Doping impurities solid solutions of donor and acceptor increases thermal and magnetothermoelectric quality factor, and to shift the maximum of thermoelectric quality factor, depending on the temperature, which enhances the operating temperature region [1-4].

It was investigated the influence of different donor and acceptor impurities, as well as sophisticated doping on the electrical and thermal properties of extruded samples of the above solid solutions. Thus experiments were carried out in samples of this size grains in which there is the best thermoelectrically quality factor [2-5].

Investigated the effect of rare earth element (REE) of gadolinium on the electrical properties of samples $Bi_{0,85}Sb_{0,15}$ solid solution in the range *77-300K* temperatures and magnetic field $74x10^4 A/m$. Extrusion samples $Bi_{0.85}Sb_{0.15}$ solid solution of gadolinium doped obtained by the technology described in [6].

2. Experimental procedure

Results for $Bi_{0.85}Sb_{0.15}$ alloy of gadolinium are shown in Figure 1. It is seen that the dependence of the electrical properties of the *Gd* concentration $Bi_{0.85}Sb_{0.15}$ not monotone: with increasing concentrations of *Gd* to 0,01at% σ of samples increases, reaches a maximum, then decreases monotonically. This concentration dependence of σ correlates well with dependency α and R_x of the *Gd* content of impurities. After heat treatment, the values of σ and R_x for all samples

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are growing and α decreases. However, the nature of these parameters depending on the concentration of *Gd* is the same as that for the samples not heat treated.

It was found that with increasing temperature of pure and impure samples to *~200÷250K*, σ of samples increases and then decreases. The exceptions are the samples containing *0.005÷0.01 at.% Gd*, the last heat treatment, which in the entire temperature range have a metallic character $\sigma(T)$. The Hall coefficient both pure and doped with *Gd* samples with increasing temperature decreases monotonically. Falls are observed in the temperature dependence of α for the pure samples and samples doped with *Gd* above *~0.01 at.%.* The unannealed samples with *0.05÷0.01 at.% Gd* in curve $\alpha(T)$ has a maximum at *140 ÷ 150 K*, and in the case of annealed samples $\alpha(T)$ is almost constant.

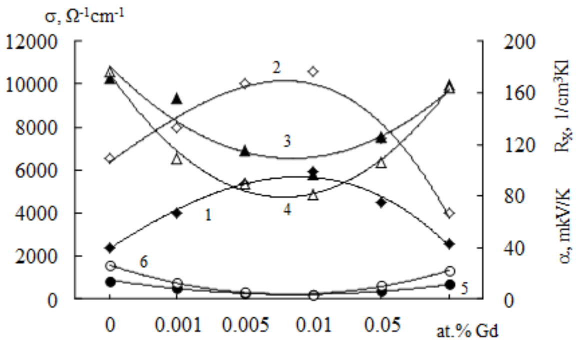

Fig. 1. Dependence of the electrical conductivity of σ (1, 2), the coefficient of thermal emf α (3, 4) and the Hall coefficient R_x (5, 6) to extruded samples $Bi_{85}Sb_{15}$ (1, 3, 5) and after (2, 4, 6) the concentration of heat treatment Gd.

These data indicate that gadolinium impurities create donor centers in $Bi_{0.85}Sb_{0.15}$. Apparently, to *0.01 at.%* gadolinium impurity atoms, being distributed uniformly patterned $Bi_{0.85}Sb_{0.15}$ lead to increased concentration of electrons in it and, therefore, increase σ and decrease α and R_x.

Greater than *0.01 at.%* gadolinium atoms either are not soluble in $Bi_{0.85}Sb_{0.15}$, or create electroneutral groups consisting of several atoms. Extremes on curves σ, α and R_x on the concentration of *Gd*, as well as the approximate values of these parameters at high concentrations of *Gd* to the values of σ and α the undoped samples $Bi_{0.85}Sb_{0.15}$ makes second assumption it more likely.

The dependence of the Hall mobility ($\mu = R_x \cdot \sigma$) extruded samples $Bi_{0.85}Sb_{0.15}$ with *Gd* doped before and after heat treatment shows that higher *110÷140 K* samples dominates the scattering of electrons by lattice vibrations [7]. Thus, to *0.01 at.%* and the smallest mobility of charge carriers prevailing dispersion of lattice vibrations starting at *140K* in which case the value of *n* depending $\mu \sim T^{n}$ is less than in pure and containing *0.1 at.% Gd* samples. For samples with *0*; *0.01* and *0.1 at.% Gd*, and the number of unsuccessful previous annealing, the value *n* is *1.9*; *1.45; 1.51* and *2.40; 1.84; 1.91*, respectively. These data indicate that at concentrations of greater than *0.01 at.%* gadolinium atoms $Bi_{0.85}Sb_{0.15}$ increasingly combined in electroneutral groups.

These assumptions are confirmed and dependencies of magnetoresistance ($\Delta\rho/\rho_0$) and the coefficient of thermal emf. ($\Delta\alpha/\alpha$) on the magnetic field intensity (Table.1).

Table 1.The dependence of the magnetoresistance ($\Delta\rho/\rho_0$), the coefficient of thermal emf. ($\Delta\alpha/\alpha$) on the magnetic field strength and the heat treatment of the extruded samples $Bi_{0,85}Sb_{0,15}$ with an admixture of gadolinium at ~77 K.

Formulations, ат.% Gd	Before annealing				After annealing			
	H=16x10⁴A/m		H=74x10⁴A/m		H=16x10⁴A/m		H=74x10⁴A/m	
	Δρ/ρ	Δα/α	Δρ/ρ	Δα/α	Δρ/ρ	Δα/α	Δρ/ρ	Δα/α
-	0,3	0,03	1,8	0,14	1,5	0,13	5,5	0,31
0,01	0,1	0,05	0,4	0,2	0,2	0,22	0,9	0,63
0,1	0,2	0,02	1,6	0,08	0,8	0,18	4.3	0,32

When exposed to the sample an external magnetic field in the direction perpendicular to the movement of electrons, charge carriers are deflected under the influence of Lorentz force. And weakly scattering, and therefore have a longer path through the free electrons will be deflected more than the strongly scattering of charge carriers. If the undoped and doped gadolinium extruded samples $Bi_{0.85}Sb_{0.15}$ at temperatures *~100÷300* by scattering by lattice vibrations prevailing at the premises of these samples in a magnetic field will increase the share of fast electrons. Accordingly, in the sample will also increase the average energy of the charge carriers. As a result, the magnetic field will increase, and the coefficient of thermal emf. Obviously, the materials which prevail other mechanisms, scattering by the magnetic field α may also decrease.

Table 2 shows the dependence of the total and the lattice thermal conductivity of extruded samples $Bi_{0.85}Sb_{0.15}$ from the lead content of impurities and gadolinium with *~90 K*. Lattice component of thermal conductivity χ_p was determined by the suppression of the electronic component of the thermal conductivity of the intermediate magnetic field [8].

The table shows that at low concentrations of impurities (up *~0.01 at.%*), χ_p of samples is approximately equal to χ_p undoped sample $Bi_{0.85}Sb_{0.15}$. This fact is true for samples are not passed, and the last best joke.

Table 2. The electrical conductivity (σ), the coefficients of the total (χ) and lattice (χ_p) constituting the heat-conductivity $Bi_{0.85}Sb_{0.15}$ extruded samples with different impurities at ~90 K

Impurity, *at.%*	Before annealing			After annealing		
	σ, *S/cm*	$\chi x10^2$, *W/(cm·K)*	$\chi_p x10^2$, *W/(cm·K)*	σ, *S/cm*	$\chi x10^2$, *W/(cm·K)*	$\chi_p x10^2$, *W/(cm·K)*
The admixture of lead						
0	3602	2,44	2,10	5250	3,02	2,41
0,0005	3460	2,40	2,09	5010	2,98	2,40
0,001	3310	2,37	2,09	4938	2,94	2,38
0,0025	2170	2,27	2,08	3241	2,77	2,41
0,05	860	2,18	2,10	1518	2,53	2,38
0,01	490	2,14	2,09	933	2,51	2,39
The admixture of gadolinium						
0,005	3805	2,67	2,09	6417	3,15	2,38
0,001	4003	2,71	2,11	8010	3,27	2,37
0,0025	4605	2,83	2,08	9110	3,44	2,39
0,005	5400	2,98	2,10	10050	3,50	2,41
0,01	5918	3,01	2,08	10595	3,60	2,40
The admixture of gadolinium (samples pre-alloyed *0.001 at.% Te*)						
0				14053	5,85	2,42
0,0005		-	-	9600	4,80	2,38
0,001		-	-	7500	4,27	2,40
0,0025		-	-	4890	3,61	2,39
0,005				4320	3,60	2,41
0,01				4030	3,40	2,39

This experimental result allows us to offer the following method for determining χ_p for extruded samples $Bi_{0.85}Sb_{0.15}$. At a temperature of *90 K*, the total thermal conductivity χ samples $Bi_{0.85}Sb_{0.15}$ consists of lattice χ_p and electronic components χ_e , ie,

$$\chi = \chi_p + \chi_e = \chi_p + L\sigma T,$$

where L is the number of Lorentz.

Annealing leads to growth χ_p, due to the healing of structural defects occurring during the extrusion.

Such violations occur during the formation of the solid solution. Therefore, during the formation of the solid solution χ greatly reduced. Because of the aforementioned considerations, solid solutions (including $Bi_{0.85}Sb_{0.15}$) low impurity concentration almost no influence on χ_p , ie thermal resistance due to phonon scattering at impurity centers low concentration significantly less than the thermal resistance caused by the scattering of phonons disorders arising from formation of a solid solution. In this case, the change of χ almost entirely due to the change of the electronic component χ_e.

Thus, it is determined that at low concentrations of impurities *(~0.01at.%)* values of the lattice thermal conductivity components do not depend on the impurity concentration. Based on this fact, it is shown that by doping the solid solutions with a sufficiently significant part of the value of electronic thermal conductivity of electroactive impurities in low concentrations can be determined lattice component of thermal conductivity [9].

Also studied the effect of impurities on the electrical lead (σ), the coefficients of thermal emf (α) and Hall (R_x) extruded samples $Bi_{0.85}Sb_{0.15}$ solid solution in a temperature range of up *~80* to *~300 K* and at magnetic fields up to ~ $74x10^4$ *A/m*.

Electrical measurements were performed along the extrusion axis DC. The data presented in Figure 2. The magnetic field has a different effect on the properties of undoped and doped with different impurities of lead samples. At the same time, in samples $Bi_{0.85}Sb_{0.15}$ doped with *0.01 at.% Pb*, at *80 K* α sign in the absence of a magnetic field and a sign of R_x in magnetic fields up to ~$9,6x10^4$ *A/m* is negative. With increasing magnetic field strength α and R_x after *H* ~ ~ $9,6x10^4$ *A/m* and $24x10^4$*A/m*, respectively, change sign from negative to positive. Apparently, at these temperatures, the hole density is insufficient to disrupt the electron-hole equilibrium. In a magnetic field the electrons are deflected stronger than the hole $(\mu_e > \mu_d)$, with the result that this sample also sign change occurs α. This explains the increase in the values of α at low temperatures under the influence of a magnetic field.

3. Results and discussions

The coefficients α and R_x sample with *0.05 at.% Pb* positive in the absence of a magnetic field, and in the whole range of changes to *H*. At temperatures above ~ *200 K* in the samples doped with different concentrations of lead, a sign of α and R_x of *H* correspond to the same dependencies for undoped sample [10].

The experimental results presented in Figure 2 is explained as follows. Atoms of lead in creating acceptor centers in $Bi_{0.85}Sb_{0.15}$, and these centers to compensate for donor centers, leading to a decrease in the concentration of electrons in the conduction band [11]. As a result, with increasing concentration of Pb electrical conductivity of $Bi_{0.85}Sb_{0.15}$ drops sharply. At low concentrations of *Pb* (up *~0.005 at.%)* samples $Bi_{0.85}Sb_{0.15}$ at *~80K* to remain purely impurity with one type of charge carriers (electrons). Therefore in them by reducing the electron density values of the coefficients α and R_x as compared to the undoped sample increase somewhat. With a further increase in the concentration of Pb due to the strong donor centers compensation patterns are close to the intrinsic conductivity of at *~80K*, which is accompanied by a decrease in the values of α and R_x, At a concentration of *0.05 at.% Pb* in the sample $Bi_{0.85}Sb_{0.15}$ is dominated hole conductivity when *~80K*, whereby the sign of α and R_x becomes positive.

In undoped samples are determined by the electrical properties of shallow donor levels. Acceptor impurities *Pb* to concentration *0.01 at.%*, offset substantially shallow donor levels. At *0.01 at.% Pb* going full compensation shallow levels. Therefore σ of sample with *0.01 at.% Pb* at ~ *80K* minimum, but with the rise in temperature in this pattern continues the ionization of deep donor levels, resulting with temperature increases σ rapidly and reaches values *200÷300K* the undoped sample. Further increase doping level leads to compensation and deep donor levels and create shallow acceptor levels. Samples with greater concentration of *0.05 atm.% Pb* have *p*-type conductivity at a temperature of about *80K* and σ more samples than *0.01 at.%* and *0.05 atm.% Pb.* As the temperature increases in the samples with a concentration of impurities greater than *0.05 at.% Pb* begins to prevail intrinsic conductivity, σ grows and becomes the electronic conductivity due to the high value of the mobility of the electrons [12].

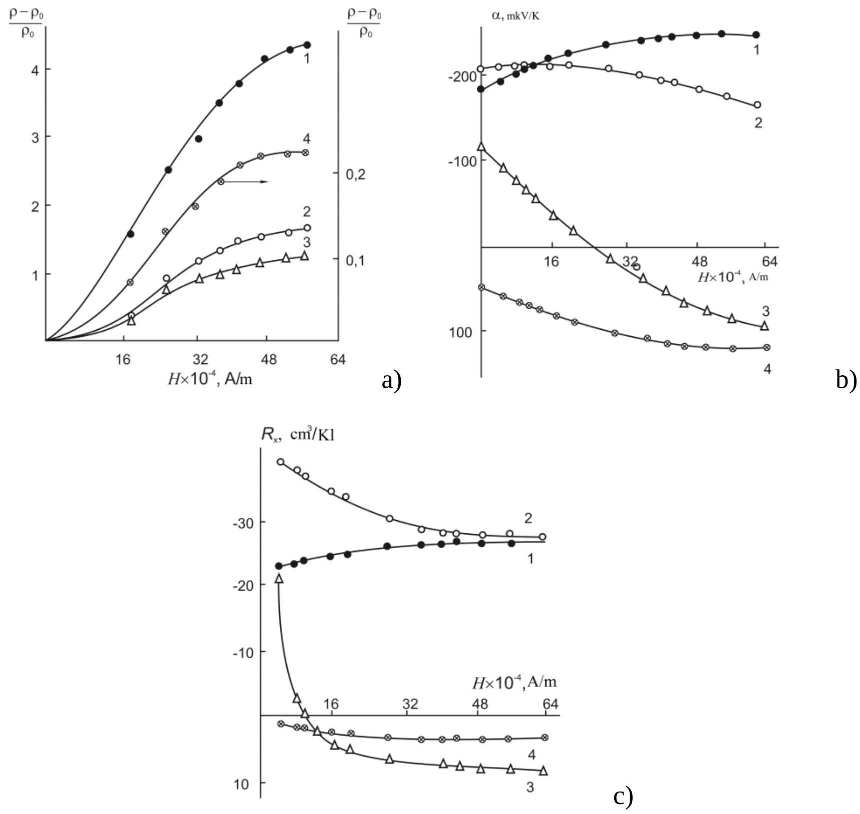

Fig. 2. Dependence of the magnetoresistance of (a), the thermal emf coefficient (b) and Hall (c) from the magnetic field strength at ~77 K for the undoped sample (1) and samples doped with 0.005 (2).; 0.01 (3), and 0.05 at.% Pb (4)

The Hall mobility of electrons in $Bi_{0.85}Sb_{0.15}$ at ~ *80K* on the order exceeds the mobility of holes. Consequently, in the magnetic field is the resistance to movement of electrons more than holes movement. As a result, with increasing concentrations of *Pb*, i.e. a decrease in the role of electrons and increasing contribution to the conductivity of the holes, σ sample from the *H* dependence weakens. Furthermore, increasing the relative proportion of the hole *H* in the overall conductivity of the conductivity at H increases. Therefore, the sample at a concentration *Pb 0,01 at.%* with increasing *H* sign coefficients α and R_x changes from negative to positive (see Fig. 2).

Samples $Bi_{0.85}Sb_{0.15}$ with *0.05 at.% Pb* with increasing temperature in the absence of the magnetic field at *~130÷140K* sign inversion occurs α and R_x from negative to positive.

In the samples $Bi_{0.85}Sb_{0.15}$ with *0.01 at.% Pb* sign inversion α and R_x from negative to positive when the magnetic field is greater than $24x10^4$ *A/m* and $9.6x10^4$ *A/m*, respectively, takes place at temperatures *~90÷100K*. This due to the fact that with increasing temperature the samples prevails intrinsic conductivity.

4. Conclusions

When exposed to a sample of the magnetic field perpendicular to the direction of motion of the electrons and holes, the charge carriers are deflected by the Lorentz force. At the same time, carriers which are less dispersed and therefore have more time free path in a magnetic field more rejected than strong dispersion carriers. The *Bi-Sb* system in the *80-300K* range is dominated by the scattering of electrons and holes by acoustic lattice vibrations, which quickly charge carriers are subject to a greater extent than slow. Therefore, when the crystal in a magnetic field to the overall fast current carriers increases and thus increasing the average energy of the charge carriers and the coefficient of thermal emf.

Thus, these results show that the extruded samples $Bi_{0.85}Sb_{0.15}$ conductivity type at low temperatures can be controlled by introducing impurities *Pb* and applying a magnetic field.

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