ELECTRICAL PROPERTIES OF SOLID SOLUTIONS OF THE Sb_2Te_3-Bi_2Te_3 SYSTEM DOPED WITH GADOLINIUM IMPURITY

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The electrical conductivity (σ), thermoelectric power (α) and Hall coefficients (R_H) of Sb_2Te_3-Bi_2Te_3 solid solutions with gadolinium impurities were studied in the temperature range of 77÷300 K. It was found that gadolinium atoms, replacing bismuth atoms that create antistructural defects, thereby reduce the concentration of charge carriers created by these defects. This mechanism is also suitable for Sb_2Te_3-Bi_2Te_3-Gd_2Te_3 compositions. At a constant amount of Sb_2Te_3, with an increase in the amount of gadolinium in the alloy, the values of electrical conductivity and charge carrier concentration decrease.

Keywords: extrusion, annealing, solid solution, extrusion, texture.

1. INTRODUCTION

The ways of increasing the efficiency of thermoelectric materials are reduced to the creation of structural defects capable of influencing to varying degrees the processes of scattering of charge carriers and phonons. The preferential reduction of thermal conductivity, compared to electrical conductivity, is currently realized by using solid solutions with isovalent substitution, in particular, $(SbBi)_2Te_3$, for low-temperature p-branches and $Bi_2(TeSe)_3$ for n-branches [1-3].

In recent years, assumptions have been made about the possibility of increasing the thermoelectric efficiency of materials with two-dimensional and three-dimensional defects of the crystal structure, the distances between which are commensurate with the mean free path of charge carriers or the wavelength of acoustic phonons responsible for heat transfer. These assumptions are based on the possibility of creating conditions under which, in areas of the material with different physical properties, there is a stronger scattering of thermal vibrations than electrons and holes.

The features and mechanisms of action of rare earth element (REE) impurities on the electrophysical and thermal properties of solid solutions based on the Bi-Te-Se and Bi-Sb-Te systems, as well as the interaction of impurities in them during complex doping, have also been studied extremely insufficiently.

Therefore, the study of physical properties, including the clarification of the mechanisms of electron and phonon transfer in $[(Sb_2Te_3)_{0.92}(Gd_2Te_3)_{0.08}]$ is an urgent task of thermoelectricity.

2. EXPERIMENTAL PART

The starting materials were antimony "Su-0000", bismuth grade "VI-000", zone-purified Te grade "T-3". All components were pre-purified.

The starting components and impurities were weighed with an accuracy of ± 0.0001 g. Samples with a low concentration of Gd were obtained by fusing a sample with a high concentration of Gd with an undoped sample. Gadolinium grade "GM-0" was used as a dopant.

The samples with an admixture of gadolinium (Gd) were synthesized in quartz ampoules evacuated to ~10^{-3} Pa at a temperature of ~ 1350 K for 12 hours. During the synthesis, the ampoule with the substance was constantly shaken. Then it was sharply cooled (by lowering it into water) to room temperature.

Electrical conductivity (σ), thermo-emf (α) and Hall (R_H) coefficients, properties of the synthesized Sb_2Te_3-Bi_2Te_3 solid solutions with gadolinium impurities were studied in the temperature range of 77÷300 K [4]. For comparison, the Bi_2Te_3 compound was also synthesized and studied. And for the Bi_2Te_3 and Sb_2Te_3 compound, the values at ~300 K were taken from the literature [5]. The Bi_2Te_3 compound was also obtained by joint alloying of the pre-purified components in a quartz ampoule evacuated to a residual pressure of ~10^{-3} Pa. The synthesis was carried out at ~950 K for three hours with continuous stirring of the melt.

3. RESULTS AND ITS DISCUSSION

The results of electrophysical parameters at ~ 77 and 300 K with a change in the amount of $[(Sb_2Te_3)_{0.92}(Gd_2Te_3)_{0.08}]$ in Bi_2Te_3 are given in the table. As can be seen, with a decrease in the amount of

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Bi_2Te_3, the electrical conductivity (σ), the concentration of charge carriers (n) and the thermoelectric coefficient (α) decrease in absolute value. In addition, at high values of the amount of Bi_2Te_3 in solid solutions, the system has n-type conductivity, and at low values (~20-26 at.%) - p-type conductivity. The values of the electrophysical parameters for the pure Bi_2Te_3 compound, indicated in the table, are in good agreement with the values given in the literature [6]. In the Bi_2Te_3 compound, the maximum temperature is shifted towards an increase in the amount of bismuth. Excess bismuth atoms, replacing mainly $Te^{(2)}$ atoms, create antistructural defects. The formation of such antistructural defects is energetically more favorable. Thus, the energy of formation of antistructural defects (~ 0.4 eV) is three times less than the energy of formation of tellurium vacancies [7]. When adding Sb_2Te_3 to bismuth telluride, the deviation from stoichiometry increases even more. As a result, the hole concentration increases, and for the $Bi_{0.5}Sb_{1.5}Te_3$ composition, the value of the thermo-emf is α=140 μV/K. On the other hand, the values of the Hall coefficients and thermo-emf obtained from measurements show that the hole mobility increases when antimony telluride is added to bismuth telluride [8].

The ionic radii of gadolinium, antimony and bismuth atoms are 1.79, 1.61 and 1.82 Å, respectively [9]. Due to the proximity of the ionic radii of gadolinium and bismuth atoms (1.79 and 1.82), it can be said that gadolinium atoms introduced into solid solutions of the composition $(Bi_2Te_3)_{1-x}(Sb_2Te_3)_x$ will primarily replace bismuth atoms. Therefore, with an increase in $[(Sb_2Te_3)_{0.92}(Gd_2Te_3)_{0.08}]$ in the Sb_2Te_3-Bi_2Te_3-Gd_2Te_3 compositions, the excess of bismuth atoms will also decrease, i.e. the concentration of charge carriers (electrons) created in the solid solution due to the excess of bismuth will decrease, and the concentration and mobility of holes will increase. As a result, the system changes from n-type conductivity to p-type conductivity.

Pure Bi_2Te_3 compound has p-type conductivity and at room temperature its electrical conductivity is 700-800 $Ohm^{-1}\cdot cm^{-1}$ [9]. With an increase in the amount of Bi_2Te_3 in the $[(Sb_2Te_3)_{0.92}(Gd_2Te_3)_{0.08}]$ - Bi_2Te_3 system, σ decreases and drops to a value of ~500 $Ohm^{-1}\cdot cm^{-1}$.

Table

Electrophysical parameters of the studied compositions

SAMPLES	AT 77 K				AT 300 K			
	σ, $Om^{-1}cm^{-1}$	α, mkV/K	n, cm^{-3}	μ, $cm^2/V\cdot c$	σ, $Om^{-1}cm^{-1}$	α, mkV/K	n, cm^{-3}	μ, $cm^2/V\cdot c$
Bi_2Te_3	4800	-77	$3{,}6\cdot10^{18}$	2223	520	-163	$3{,}6\cdot10^{18}$	947
Sb_2Te_3		_	_	_	718	106	$9\cdot10^{18}$	490
$[(Sb_2Te_3)_{0,92}(Gd_2Te_3)_{0,08}]_{0,05}[Bi_2Te_3]_{0,95}$	4652	-53	$1{,}5\cdot10^{20}$	221	1248	-120,6	$1{,}25\cdot10^{20}$	62
$[(Sb_2Te_3)_{0,92}(Gd_2Te_3)_{0,08}]_{0,10}[Bi_2Te_3]_{0,90}$	3543	-65	$7{,}6\cdot10^{19}$	205	944	-130	$1{,}04\cdot10^{20}$	57
$[(Sb_2Te_3)_{0,92}(Gd_2Te_3)_{0,08}]_{0,15}[Bi_2Te_3]_{0,85}$	3058	-71	$6{,}3\cdot10^{19}$	201	760	-139	$9{,}1\cdot10^{19}$	51
$(Sb_2Te_3)_{0,72}(Gd_2Te_3)_{0,02}(Bi_2Te_3)_{0,26}$	1240	82	$2{,}4\cdot10^{18}$	885	650	200	$2{,}4\cdot10^{18}$	440
$(Sb_2Te_3)_{0,74}(Bi_2Te_3)_{0,24}(Gd_2Te_3)_{0,02}$	1100	69	$2{,}7\cdot10^{19}$	240	255	165	$2{,}8\cdot10^{19}$	61
$(Sb_2Te_3)_{0,74}(Bi_2Te_3)_{0,20}(Gd_2Te_3)_{0,06}$	220	40	$2{,}5\cdot10^{19}$	63	110	105	$2{,}4\cdot10^{19}$	32

At 77 K, the ratio increases even more and reaches a value of ~3. This indicates that an increase in σ and a decrease in the concentration of charge carriers n in the $[(Sb_2Te_3)_{0.92}(Gd_2Te_3)_{0.08}]$ compositions are associated with the influence of gadolinium. It can be assumed that gadolinium atoms, replacing bismuth atoms that create antistructural defects, thereby reduce the concentration of charge carriers created by these defects. This mechanism is also suitable for the Sb_2Te_3-Bi_2Te_3-Gd_2Te_3 compositions. Moreover, here, with a constant amount of Sb_2Te_3, with an increase in the amount of gadolinium in the alloy, the values of electrical conductivity and charge carrier concentration decrease.

The temperature dependences of the electrophysical parameters (σ and α) for the studied compositions are shown in Fig. 1, 2. As can be seen from the figures, for all curves the σ (T), α (T) dependences have a metallic character - with an increase in temperature, σ decreases, α increases, and the Hall coefficient does not change with temperature.

According to the temperature dependence of the Hall coefficient in the temperature range of 77-300K, the concentration of charge carriers is 10^{18}-10^{20} cm^{-3} and does not change with temperature. The indicated temperature dependences of electrical conductivity and the Hall coefficient are characteristic of partially degenerate semiconductors.

The temperature dependence of the Hall mobility $\mu = R_H\sigma$shows that in the specified compositions in the temperature range of 77-300 K the charge carriers are scattered mainly by acoustic lattice vibrations (phonons). Fig. 3 shows the dependence of the magnetoresistance on the magnetic field strength for the specified compositions. As can be seen, only for the composition $(Sb_2Te_3)_{0.72}(Bi_2Te_3)_{0.26}(Gd_2Te_3)_{0.02}$ a non-zero magnetoresistance is observed. This indicates that this composition is a non-degenerate semiconductor, while the other compositions are degenerate semiconductors.

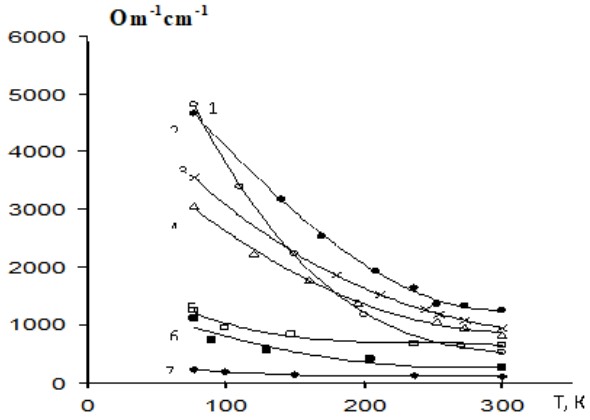

Fig. 1. Temperature dependences of electrical conductivity.
1-$[(Sb_2Te_3)_{0,92}(Gd_2Te_3)_{0,08}]_{0,05}[Bi_2Te_3]_{0,95}$, 2- $[(Sb_2Te_3)_{0,92}(Gd_2Te_3)_{0,08}]_{0,10}[Bi_2Te_3]_{0,90}$,
3- $[(Sb_2Te_3)_{0,92}(Gd_2Te_3)_{0,08}]_{0,15}$ $[Bi_2Te_3]_{0,85}$,4-$(Sb_2Te_3)_{0,74}(Bi_2Te_3)_{0,24}$ $(Gd_2Te_3)_{0,02}$,
5-$(Sb_2Te_3)_{0,72}(Bi_2Te_3)_{0,26}(Gd_2Te_3)_{0,02}$,6- $(Sb_2Te_3)_{0,74}(Bi_2Te)_{0,20}(Gd_2Te_3)_{0,06}$, 7- Bi_2Te_3

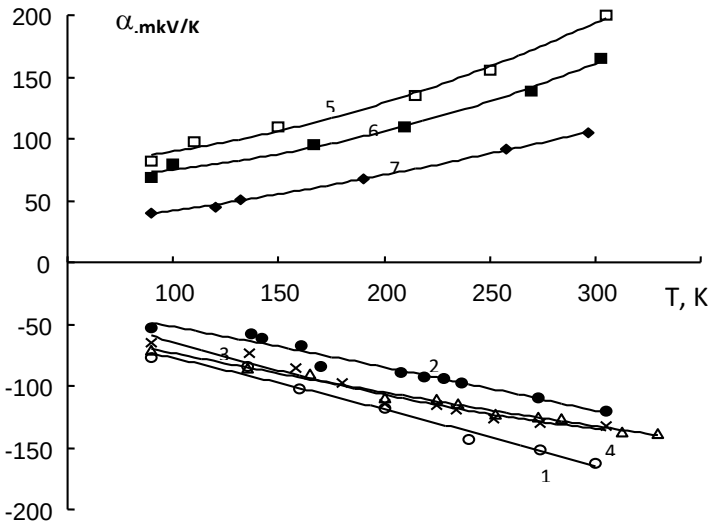

Fig. 2. Temperature dependences of the thermoelectric coefficient. The designations are the same as in Fig. 1.

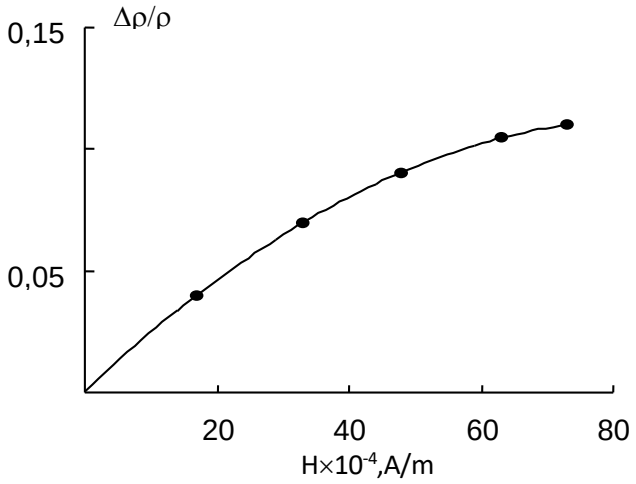

Fig. 3. Dependence of specific resistance on magnetic field strength.

The analysis of the obtained experimental data shows that for the specified composition the dependence $\frac{\Delta\rho}{\rho_0} \sim B^2$ is in good agreement with the value of A for the case of scattering on lattice vibrations.

Taking into account the above, taking A=1.18 for samples of the composition Bi_2Te_3 and $(Sb_2Te_3)_{0.72}(Gd_2Te_3)_{0.02}(Bi_2Te_3)_{0.26,}$ and A=1 for other compositions, the concentrations of electrons (for n-type samples) and holes (for p-type samples) were calculated (Table).

The mobilities of electrons and holes were calculated using the values of the Hall coefficient and electrical conductivity from the expression $\mu=P_H\cdot\sigma$. For this purpose, in order to increase the accuracy, we used the Hall coefficient values for the samples measured at ~ 77 K. Since the charge carrier mobility at~77 K is higher than the mobility at ~300 K, the Hall coefficient is measured with greater accuracy at low temperatures. Taking into account the fact that the charge carrier concentration determined at 77 K does not change down to room temperature, the charge carrier mobility was calculated in the temperature range of 77÷300 K. It was found that for all compositions, starting from ~ 77 K, the mobility decreases with increasing temperature according to the law $\mu \sim T^{-n}$ (for both electrons and holes). The value of the temperature index n changes from 1.65 (for Bi_2Te_3 samples) to ~ 1.35. This indicates that in the range of ~ 77÷300 K in the indicated compositions, electrons and holes are scattered mainly by thermal vibrations of the lattice. Such a scattering mechanism also results from the magnetoresistive effect.

It is evident that with the increase of the amount of gadolinium in the compositions the mobility of electrons and holes decreases sharply (except for the composition $(Sb_2Te_3)_{0.72}(Gd_2Te_3)_{0.02}(Bi_2Te_3)_{0.26}$). The reason for this is the increase of scattering of electrons and holes with the formation of a triple system. It can also be assumed that the effective cross-section of scattering centers for electrons and holes created by gadolinium atoms is of sufficiently great importance. Thus, as already noted above, with the addition of Sb_2Te_3 to Bi_2Te_3 the mobility of holes increases.

4. CONCLUSION

Thus, it was found that gadolinium atoms, replacing bismuth atoms that create antistructural defects, thereby reduce the concentration of charge carriers created by these defects. This mechanism is also suitable for Sb_2Te_3-Bi_2Te_3-Gd_2Te_3 compositions. At a constant amount of Sb_2Te_3, with an increase in the amount of gadolinium in the alloy, the values of electrical conductivity and concentration of charge carriers decrease. With an increase in the amount of gadolinium in the compositions, the mobility of electrons and holes also decreases sharply (with the exception of the composition $(Sb_2Te_3)_{0.72}$ $(Gd_2Te_3)_{0.02}$ $(Bi_2Te_3)_{0.26}$). The reason for this is an increase in the scattering of electrons and holes with the formation of a ternary system. It can also be assumed that the effective cross section of the scattering centers for electrons and holes created by gadolinium atoms is quite significant.

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