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**THERMOELECTRIC AND MECHANICAL PROPERTIES  
OF  $(Bi_{1-x}Sb_x)_2Te_3$  ( $x = 0 \div 0.07$ ) SEMICONDUCTOR SOLID SOLUTIONS**

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*The dependences of thermoelectric properties and microhardness on the composition of polycrystalline  $(Bi_{1-x}Sb_x)_2Te_3$  solid solutions in the concentration range  $x = 0 \div 0.07$  at room temperature were investigated. A drastic growth of microhardness was discovered with a simultaneous reduction of the Hall coefficient, the Seebeck coefficient and electric conductivity with increase in antimony content  $x = 0.005 - 0.01$ , following which with further increase in  $x$  to  $x = 0.01 - 0.015$ , the type of the dependences was reversed. The observed effect is attributable to a high degree of crystal lattice disorder with the introduction of the first portions of impurity and to subsequent relaxation processes with formation of percolation channels in crystal impurity subsystem. With further increase in  $x$ , the Hall coefficient and the Seebeck coefficient practically do not change with composition, and the observed more complicated dependence of microhardness and electric conductivity on  $x$  is interpreted as a manifestation of short-range processes in a solid solution.*

**Key words:**  $(Bi_{1-x}Sb_x)_2Te_3$  solid solution, composition, room temperature, thermoelectric properties, microhardness, percolation.

## Introduction

Today semiconductor solid solutions of bismuth and antimony telluride  $(Bi_{1-x}Sb_x)_2Te_3$  are among the most efficient thermoelectric (TE) materials widely used for the purposes of TE cooling at close to room temperatures [1 – 4].

The  $Bi_2Te_3$  and  $Sb_2Te_3$  compounds and a continuous series of  $(Bi_{1-x}Sb_x)_2Te_3$  solid solutions between them crystallize in a rhombohedral lattice of tetradymite type based on a nine-layer package of  $Bi(Sb)$  and  $Te$  atoms and characterized by considerable anisotropy of properties. To describe the zone structure of these compounds, use is usually made of a six-ellipsoid model of isoenergetic surface with ellipsoid centres on symmetry planes, which is in fairly good agreement with the experimental data [1 – 5]. The maximum on the liquidus and solidus curves close to  $Bi_2Te_3$  compound in  $Bi-Te$  system is shifted from stoichiometric composition towards  $Bi$  excess and at congruent melting temperature corresponds, according to different authors, to compositions: 59.935 at %  $Te$  [6], 59.95 at %  $Te$  [7] and 59.8 at %  $Te$  [8].

The data of various authors regarding the boundaries of  $Bi_2Te_3$  homogeneity area at high temperatures (700 – 850 K) are in good agreement with each other: (59.4 – 59.92) – (60.05 – 60.35) at %  $Te$  [2, 6 – 9]. The range of  $Bi_2Te_3$  homogeneity area in  $Bi-Te$  system, determined in [10] for the samples prepared by the procedure similar to that used here corresponded to 59.5 – 61 at %  $Te$ . The basic types of defects in stoichiometric  $Bi_2Te_3$  and  $Sb_2Te_3$  and  $(Bi_{1-x}Sb_x)_2Te_3$  solid solutions are antisite defects  $Bi_{Te}$  and  $Sb_{Te}$ , formed by substitution of tellurium vacancies by  $Bi$  and  $Sb$  atoms [6, 11]. In [10] it was shown that with a deviation from stoichiometric composition (60 at %  $Te$ )

both toward *Bi* excess and *Te* excess there is growth of microhardness  $H$  and electric conductivity  $\sigma$  and drop of the Seebeck coefficient  $S$  and the Hall coefficient  $R_H$  which was attributed by the authors [10] to introduction to crystals of nonstoichiometry defects increasing carrier concentration and the level of stress in the lattice. It was established that with stoichiometric composition (60 at % *Te*) and with a deviation from it toward *Bi* excess the *p*-type conductivity is observed.

In recent years it has been established that  $Bi_2Te_3$  and  $Sb_2Te_3$  compounds refer to a new class of objects in solid state physics, namely 3D-topological insulators, where strictly spin-oriented surface electrons are not scattered by defects and can move along the surface of the bulk material almost without energy loss. Thanks to protection of surface states, the topological insulators hold good promise for practical applications in spintronics, quantum computers, thermoelectricity and other fields [12 – 14]. As long as it is rather difficult to single out the contribution to conductivity of surface layer, one of the tasks is to reduce the contribution to conductivity of the bulk component, which can be done by doping of material in order to reduce charge carrier concentration. Therefore, the works studying the effect of impurities on carrier concentration in  $Bi_2Te_3$  and  $Sb_2Te_3$  are of current interest.

Studies of TE properties of *Bi-Sb-Te* ternary system in the cut of  $Bi_2Te_3$ - $Sb_2Te_3$  were performed by many authors (see, for instance, [15 – 22]). However, practically in all the works the samples were made with a big step of impurity component concentration, which prevented from making a thorough investigation of properties behaviour with composition.

Earlier in many works (see, for instance, [23 – 32]) for a number of semiconductor and semimetallic solid solutions it was discovered that in the area of low impurity content (up to ~ 1 at %) the concentration anomalies were observed on the composition dependences of properties. The authors of these works attributed these peculiar properties to the fact that in going from dilute to concentrated solid solutions there is phase transition of percolation type, accompanied by critical phenomena and having a universal character, i.e. inherent in any solid solutions [31, 32]. As long as the presence of phase transition generally results in considerable change of properties, it is very important to take this effect into account in the development of efficient TE materials, since one of the main ways for modification of TE material properties is formation of solid solutions and doping.

When using semiconductor materials in TE devices, certain demands are placed on mechanical properties. Doping for the purpose of improving TE figure of merit is accompanied by modification of not only thermoelectric, but also mechanical properties, and the character of this modification should be known. One of informative mechanical characteristics is microhardness, i.e. characteristic of material strength under conditions of combined stress arising at introduction of indenter [33]. As long as between  $H$  and other mechanical characteristics of crystal there is a definite link, by the value of  $H$  one can estimate the value of hardening without taking tension (compression) – stress diagram.

In connection with the above, it was interesting to study TE and mechanical properties depending on the composition of  $(Bi_{1-x}Sb_x)_2Te_3$  solid solutions prepared under identical process conditions, in the area of low content of the second component. As the object of study,  $(Bi_{1-x}Sb_x)_2Te_3$  solid solution in the concentration range  $x = 0 \div 0.07$  was chosen, and as the properties under study –  $H$ ,  $R_H$ ,  $S$  and  $\sigma$ .

From the results obtained in this paper it follows that with a detailed study of the properties of polycrystalline cast samples of  $Bi_2Te_3$  solid solutions in  $(Bi_{1-x}Sb_x)_2Te_3$  system one can find concentration anomalies of properties in the range of low concentrations of introduced impurity component ( $Sb_2Te_3$ ).

## Experimental procedure

Polycrystalline cast samples of  $(Bi_{1-x}Sb_x)_2Te_3$  ( $x = 0 - 0.07$ ) solid solutions with concentration step  $\Delta x$  from 0.0025 to 0.01 were obtained from high-purity (at least 99.999 % of basic component) elements (*Bi*, *Sb* and *Te*) by melting them in evacuated to  $10^{-3}$  Pa quartz ampoules at temperature  $(1020 \pm 10)$  K, holding in the melt for 5 hours with the use of vibratory agitation, cooling to temperature  $(650 \pm 10)$  K, holding at this temperature for 300 hours for homogenization of alloys and obtaining compositionally uniform ingots and subsequent cooling at a rate of switched off furnace. All 20 samples of various compositions were synthesized and subject to thermal treatment simultaneously, during one process cycle, which assured the identity of their preparation conditions and the possibility of comparing the properties of samples of various compositions.

Quantitative chemical analysis of obtained samples was performed by the methods of X-ray fluorescent analysis and electron-microprobe analysis. X-ray fluorescent analysis was conducted on X-ray fluorescent spectrometer SPRUT. The area of irradiated surface was  $\sim 12$  mm<sup>2</sup>. The accuracy of the method was  $\approx 0.2 - 0.5$  %. Electron microprobe analysis was conducted on scanning electron microscope JSM-6390LV (Jeol Ltd., Japan), with a system of energy-dispersive spectrometer INCA Energy 350 (Oxford Instruments Analytical Ltd., Great Britain). Control weighing of ingots after synthesis and thermal treatment, as well as the above set of quantitative chemical analysis methods showed that the deviation of alloy composition from the calculated one in all the elements did not exceed  $\Delta x = 0.0002$ .

The degree of uniformity of obtained samples was also controlled by methods of local measurements of  $H$  and  $S$  on the samples cut of the same ingot in two mutually perpendicular directions. The size of microprobe for measurement of  $S$  was  $\approx 100$   $\mu$ m, and the size of print in the measurement of  $H$  did not exceed  $\approx 10$   $\mu$ m. The spread in the values of measured parameters in the sample did not exceed their measurement error, which, on the one hand, pointed to isotropy of polycrystalline material, and, on the other hand, to its uniformity.

Microhardness  $H$  was measured at room temperature on PMT-3 instrument using a diamond pyramid under load  $P = 0.49$  N. The choice of load value was made by constructing the dependences  $H(P)$  for each sample and determining the value of  $P$  following which  $H$  ceases to depend on  $P$ . It was established that microhardness decreases with an increase in  $P$  (a scale effect takes place), but the values of  $H$  are practically independent of  $P$ , starting from  $P = 0.49$  H, and under these conditions  $H$  is an objective characteristic of sample strength properties. The times of loading, holding under load and load removal made 10 s. Adjustment of the instrument was done with the aid of freshly cleaved *NaCl* crystals. The values of  $H$  were obtained as the arithmetical mean when measuring 30 prints. Statistical treatment of measured results showed that the value of relative mean-square fluctuation of a series of 30  $H$  measurements did not exceed 2 – 3 %. Determination of  $\sigma$  and  $R_H$  to an accuracy not less than  $\pm 5$  % was performed using the van der Pauw method with magnetic field induction  $B = 1$  T. The Seebeck coefficient was measured by compensation method with respect to copper electrodes to an accuracy of  $\pm 3$  %. The concentration of charge carriers (holes)  $p$  was calculated by the formula  $p = r/(e \cdot R_H)$ , assuming that the Hall factor is  $r = 1$ .

With a strong degeneracy (which takes place in this case) a relation between carrier concentration and the Seebeck coefficient is expressed by the formula [3]

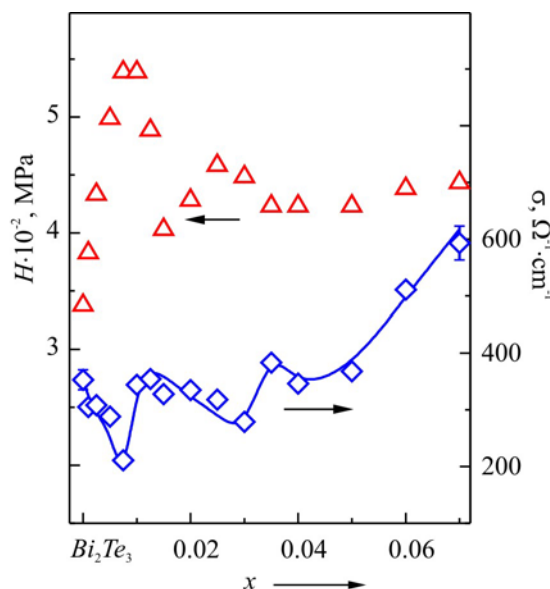
$$S = \left( \delta + \frac{3}{2} \right) \frac{2\pi^{2/3} k^2 T m^*}{3^{5/3} e \hbar^2 p^{2/3}}, \quad (1)$$

where  $m^*$  is effective mass;  $p$  is charge carrier concentration;  $\delta$  is coefficient depending on scattering mechanism (for  $(Bi_{1-x}Sb_x)_2Te_3$  solid solutions  $\delta = 0$  [3]). From formula (1) by the obtained value of  $S$  for  $Bi_2Te_3$ , taking into account that  $m^* = 0.34 m$  [3] and  $T = 300$  K, one can obtain the concentration of charge carriers (holes). The calculated value of  $p$  ( $p = (1.25 \pm 0.05) \cdot 10^{19} \text{ cm}^{-3}$ ) for  $Bi_2Te_3$  is in good agreement with the value of  $p$  measured by the Hall effect method, as well as with the data reported in the literature. The same situation was observed for all investigated alloys.

The value of TE power  $P$  was determined by the formula  $P = S^2\sigma$ .

### Experimental results

Fig. 1 shows the composition dependence of  $H$  which is apparently of a complex type. On introducing to  $Bi_2Te_3$  of the first portions of  $Sb_2Te_3$  up to  $x = 0.0075$  there is a sharp (almost 1.5 times) increase in  $H$ . With a further increase of  $x$  to  $x = 0.015$ , microhardness drastically drops to the value close to  $H$  value of the initial component ( $Bi_2Te_3$ ). Later, with increase in  $x$ , there is again growth of  $H$  to  $x = 0.025$ , following which  $H$  is reduced to  $x = 0.04$ . In the composition range  $x = 0.04 \div 0.07$  there is a minor increase in microhardness. The type of the dependence  $H(x)$ , unusual for solid solutions, points to qualitative changes in crystal defective subsystem with increasing concentration of  $Bi$ . Note that  $H$  value of the initial bismuth telluride ( $H = 0.35 \pm 0.01$  GPa) is somewhat lower than the values cited in a number of papers for single crystals and polycrystals (0.5 – 0.95 GPa) [34 – 37]. The difference may be due to the difference in sample manufacturing technique and, accordingly, their structural state, the methods for measuring  $H$  (for instance, different load on the indenter), the quality of sample surface preparation for measuring  $H$ . Moreover, in [10] it was shown that TE properties and microhardness are extremely sensitive to deviation from stoichiometric composition which is matched by minimum  $H$  values and maximum  $S$ ,  $\sigma$  and  $R_H$  values.



*Fig. 1. Dependences of microhardness  $H$  and electric conductivity  $\sigma$  on composition  $x$  of polycrystalline  $(Bi_{1-x}Sb_x)_2Te_3$  solid solutions at 300 K.*

All samples under study had  $p$ -type conductivity, just as the initial polycrystal of stoichiometric  $Bi_2Te_3$ . Fig. 2 shows the dependences  $R_H(x)$  and  $S(x)$ . It can be seen that the type of the dependences is similar for both kinetic coefficients: in the range  $x = 0 \div 0.005$  there is a decrease in  $R_H$  and  $S$  values, then up to  $x = 0 \div 0.01$  they increase and further  $R_H$  and  $S$  values are practically unchanged.

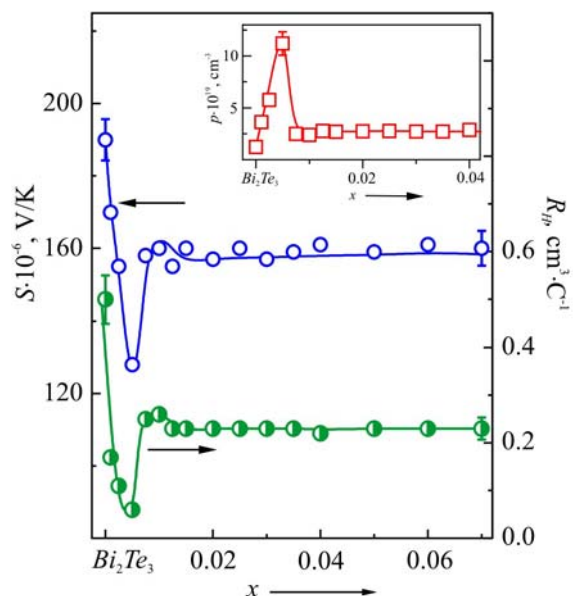


Fig. 2. Dependences of the Seebeck coefficient  $S$  and the Hall coefficient  $R_H$  on composition  $x$  of polycrystalline  $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$  solid solutions at 300 K. The inset: Dependence of hole concentration  $p$  on composition  $x$  of  $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$  solid solutions at temperature 300 K.

By the  $R_H$  values, on the assumption of one sort of charge carriers, the hole concentration  $p$  was calculated, the composition dependence of which is given in the insert to Fig. 2. With increase in  $x$  to  $x = 0.005$ , the value of  $p$  grows, increasing by almost an order, then up to  $x = 0.01$  – drops, following which it is practically unchanged. The simplest calculation shows that in the area  $x = 0 \div 0.005$  each antimony atom which substitutes  $\text{Bi}$  atom introduces additionally  $(0.65 \pm 0.05)$  charge carriers (holes).

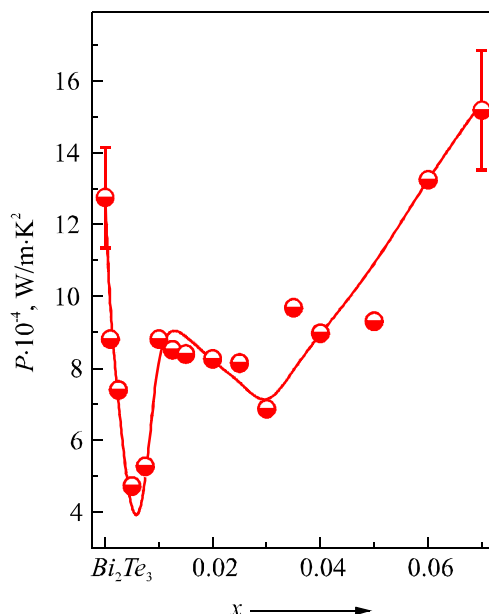


Fig. 3. Dependence of thermoelectric power  $P = S^2 \cdot \sigma$  on composition  $x$  of polycrystalline  $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$  solid solutions at 300 K.

Electric conductivity changes with composition in a complicated way (Fig. 1). At first, on introducing of  $\text{Sb}_2\text{Te}_3$  (up to  $x = 0.0075$ ),  $\sigma$  drastically decreases, then in the range

$x = 0.0075 \div 0.0125$  there is growth of electric conductivity, following which  $\sigma$  again drops to  $x \sim 0.03$  and then grows up to  $x = 0.07$ . The composition dependence of TE is of similar type (Fig. 3).

From the obtained experimental data it follows that the dependences of properties on the composition of  $(Bi_{1-x}Sb_x)_2Te_3$  solid solutions in the concentration range adjacent to bismuth telluride are of a pronounced non-monotonic type.

### Discussion of the results

As long as  $Sb_2Te_3$  compound is isovalent and isomorphic impurity for  $Bi_2Te_3$ , and both compounds form a continuous series of solid solutions, it might be expected that the composition dependences of various properties will represent smooth curves. Such assumption agrees with the data from a number of works [17 – 22] which indicated a continuous decrease of  $R_H$  and  $S$ , as well as growth of  $\sigma$  in going from  $Bi_2Te_3$  to  $Sb_2Te_3$ . However, these works studied few alloys of different composition over a wide concentration range. Therefore, a complex type of concentration dependences of properties discovered in this paper in the range  $x = 0 \div 0.07$  demands explanation.

It is known that introduction of impurity forming a solid solution is practically always accompanied by  $H$  increase. The theories of solid solution strengthening generally deal with a case of dilute solid solutions and show that the composition dependence of  $H$  is close to linear [38 – 40]. From the standpoint of modern concepts, mechanical properties of crystal are largely determined by dislocation mobility [38], and the root cause for strengthening is elastic interaction of dislocations with the dissolved impurity atoms which block dislocation motion. In the region of dilute solid solutions the elastic deformation fields created by individual impurity atoms practically do not overlap, each impurity atom introduces an additive contribution to  $H$  value, and the main parameters governing the degree of change in  $H$  are concentrations of point defects and the bonding energy of point defect and dislocation. The elastic interaction between dislocations and impurities leads to reduction of dislocation mobility and, hence, to strengthening. So, growth of  $H$  with the introduction of the first portions of  $Sb_2Te_3$  (to  $x = 0.0075$ ) does not require special explanation. However, a drastic drop of  $H$  at  $x = 0.0075$ , pointing to a change in the character of dislocation motion, increase of their mobility and crystal weakening, cannot be explained within the theories of solid solution strengthening.

In a number of earlier works by one of the present authors, weakening defect was discovered in the region of low impurity concentrations [23, 26, 29, 31 – 32] and within percolation theory [41 – 42] weakening mechanism was proposed related to collective interaction of deformation fields of impurity atoms, when concentration of the latter reaches percolation threshold – critical value of  $x_c$  corresponding to formation of “infinite cluster” – a single chain of overlapping deformation fields that penetrates crystal. Formation of “infinite cluster” on achievement of percolation threshold  $x_c$  can be regarded as a phase transition accompanied by critical phenomena.

Assuming that composition with  $x = 0.005$  corresponds to percolation threshold, and using the conclusions obtained from solving the problem of spheres of percolation theory [41 – 42], one can estimate the size of deformation sphere  $R_0$  by the formula:

$$\frac{4}{3}\pi N_c (2R_0)^3 \approx 2.7, \quad (2)$$

where  $N_c$  is the number of sphere centres in the unit volume with the composition of  $(Bi_{1-x}Sb_x)_2Te_3$  solid solution corresponding to percolation threshold ( $x = x_c$ ). Simple calculation shows that  $R_0 = (2.7 \pm 0.05) a_0$ , where  $a_0$  is quasi-cubic parameter of  $Bi_2Te_3$  unit cell, which agrees with the short-range character of deformation interaction.

A sharp increase in hole concentration with small additions of  $Sb_2Te_3$  ( $x = 0 - 0.005$ ) and a simultaneous drastic increase in  $H$  and decrease of  $\sigma$  testify to considerable deformation of crystal lattice and the appearance of additional electrically active centres. In this connection, it can be assumed that the first portions of  $Sb_2Te_3$  do not enter crystal lattice by the mechanism of simple cationic substitution, and formation of solid solution is accompanied by the appearance of additional antisite defects. Because of deviation from stoichiometry toward  $Bi$  excess (the maximum on fusion curves in  $Bi-Te$  system is shifted from stoichiometric composition), the stoichiometric  $Bi_2Te_3$  comprises a certain equilibrium concentration of defects, mainly antisite  $Bi_{Te}$  defects. With the introduction to bismuth telluride of the first portions of  $Sb_2Te_3$ , conditions of thermodynamic equilibrium change, which can lead to increase in equilibrium concentration of antisite defects in  $Bi_2Te_3$ . From the thermodynamic standpoint for the emerged  $Sb$  it is more favourable to occupy antisite positions, owing to which hole concentration increases. However, it is valid so long as antimony atoms practically do not interact with each other. After formation of percolation channels the situation changes and interaction energy begins to contribute to the expression for free energy, changing thermodynamic equilibrium conditions and leading to a decrease in the equilibrium concentration of defects.

This assumption is supported by the fact that in the concentration range  $x = 0 - 0.005$  each  $Sb$  atom supplies  $(0.65 \pm 0.05)$  holes, which corresponds to formation of acceptor-type antisite defects ( $Bi_{Te}$  or  $Sb_{Te}$ ) [43]. It is also noteworthy that increase in the assortment and number of structural defects with a low impurity content, when interaction of impurity atoms between each other can be ignored, is stimulated by a sharp increase in configuration entropy, which with the introduction of the first portions of impurity is not compensated by simultaneous growth of crystal internal energy. As long as bonding energy of impurity atom is less than that of the host atom (at least in the region of low impurity concentration), the antisite defects will be primarily formed by impurity atoms.

Achievement of percolation threshold stimulates self-organization processes in the subsystem of defects which in the presence of corresponding thermodynamic stimuli can lead to formation of ordered phase. In this case the weakening effect must be particularly significant. A sharp decrease in  $H$  and  $p$  with a simultaneous growth of  $\sigma$  suggest that ordering processes in all likelihood take place.

After passing of crystal to a qualitatively new state related to formation of percolation channels ("impurity condensate"), new centres appear that impede dislocation motion, and  $H$  again grows with increase in antimony concentration.

Further increase in  $x$  increases the likelihood of Coulomb interaction between the introduced unlike charged ions  $Sb^{+3}$  and  $Te^{+2}$  which stimulates the process of chemical interaction with formation of electrically neutral  $Sb_2Te_3$  complexes. As long as the concentration of complexes is low, they do not interact with each other, but as their concentration increases, flow channels are formed in the crystal through the resulting complexes. The presence of the second anomalous portion of  $H$  drop and  $\sigma$  growth with increase in  $x$  in the range  $x = 0.025 - 0.04$  can be related to achievement of "complex formation threshold", when flow channels through neutral molecular complexes  $Sb_2Te_3$  are formed, leading to a qualitative change of properties [44].

Thus, the composition dependences of both  $H$  and TE properties testify to complex defect forming processes taking place in  $Bi_2Te_3$  crystal lattice with the introduction of  $Sb_2Te_3$ .

One should take into account possible influence of kinetic factors. For a long time (300 hours) the alloys were annealed at 650 K, with high probability of their coming to a state close to equilibrium at this temperature, following which they were cooled to temperature 300 K at a rate of furnace turned

off. Taking into account low diffusion rate at close to room temperatures and low concentration of impurity atoms not interacting with each other, it can be assumed that in the range of the lowest concentrations of impurity component, in view of incompleteness of diffusion processes, high-temperature states are recorded that correspond to annealing temperature and are oversaturated with defects. In this case, formation of percolation channels can drastically increase the rate of diffusion processes and transfer the alloy oversaturated with defects to a more equilibrium state. A sharp decrease in  $H$  and a sharp increase in  $R_H$ ,  $S$  and  $\sigma$  with  $x$  increase above  $x = 0.01 - 0.015$  may indicate transition to equilibrium state from the nonequilibrium state formed as a result of oversaturation with defects and freezing of high-temperature state after accelerated cooling of alloys at a rate of furnace turned off. Therefore, it is desirable to study the effect of ageing processes on the properties of  $(Bi_{1-x}Sb_x)_2Te_3$  solid solutions in the range of low concentration of  $Sb_2Te_3$  in order to reveal the role of kinetic factors in the character of manifestation of percolation effects.

## Conclusion

Analysis of the results of detailed investigation of the composition dependences of thermoelectric and mechanical properties of polycrystalline  $(Bi_{1-x}Sb_x)_2Te_3$  ( $x = 0 - 0.07$ ) solid solutions has shown that the concentration dependences of microhardness, the Seebeck coefficient, the Hall coefficient, electric conductivity and thermoelectric power are of a pronounced non-monotonic type.

A drastic increase in microhardness and carrier concentration with a simultaneous decrease in the Seebeck coefficient and electric conductivity values with the introduction of the first impurity portions (up to  $x = 0.005 - 0.01$ ) is related to high degree of crystal lattice disorder and increase in the concentration of antisite defects, and the reversal of the type of the dependences with further increase in  $x$  – to change in thermodynamic equilibrium conditions on achievement of percolation threshold and formation of “infinite cluster”. It is assumed that this percolation-type transition from dilute to concentrated solid solutions is accompanied by self-organization processes in crystal impurity subsystem.

Anomalies on the concentration dependences of microhardness and electric conductivity in the range  $x = 0.025 - 0.04$  are connected with transition to associated solid solutions.

An assumption was made on the influence of kinetic factors on the type of composition-property dependence at low impurity concentrations because of the possibility of freezing high-temperature states corresponding to annealing temperature as a result of rapid cooling to room temperature and insufficient time for completion of diffusion processes.

The obtained results prove the earlier assumptions on the universal character of solid solutions behaviour in the low concentration range of impurity component – the presence of concentration anomalies of properties related to transition from dilute to concentrated solid solutions. The discovered effects must be taken into account in the development of methods for improving the thermoelectric efficiency of materials by forming solid solutions and doping.

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