

E. I. Rogacheva¹, A. V. Budnik¹, O. S. Vodorez¹, M.V. Dobrotvorskaya²

¹National Technical University “Kharkiv Polytechnic Institute”,
21 Frunze St., Kharkiv 61002, Ukraine

²Institute for Single Crystals of NAS of Ukraine,
60 Prospect Lenin, Kharkov, 61001, Ukraine

**THE EFFECT OF DEVIATION FROM STOICHIOMETRY ON
THERMOELECTRIC AND MECHANICAL PROPERTIES OF Bi_2Te_3**

For alloys in the Bi-Te system with compositions in the vicinity of Bi_2Te_3 (57.5-70 at.% Te), room temperature dependences of the Seebeck coefficient S , the Hall coefficient R_H , electrical conductivity σ , charge carrier mobility μ , thermoelectric power factor P , and microhardness H on Te concentration were measured. The objects of the study were polycrystalline samples prepared by an ampoule method and subjected to a long-term homogenizing annealing at 670 K. It was found that under the deviation from the stoichiometric composition (60 at.% Te) to the Bi side down to 57.5 at.% Te and to the Te side up to ~ 61 at.% Te, S , R_H , μ decrease, whereas H increases; at ~ 61 at.% Te the inversion of the conductivity type $p \rightarrow n$ occurs, and at the inversion point the minimum values of σ and μ are observed. In the region corresponding to the electron conductivity, in the vicinity of 63 at.% Te, extrema are observed in the property-composition dependences, and starting from ~ 65 at.% Te, S , R_H and μ remain practically constant, while H increases monotonically. The maximum values of P correspond to the stoichiometric composition (p-type conductivity) and to 65 at.% Te (n-type conductivity). Possible causes of such non-monotonic behavior of the properties under deviation from the stoichiometric composition are discussed.

Key words: bismuth telluride, nonstoichiometry, thermoelectric properties, microhardness

Introduction

Deviation from stoichiometry belongs to one of the basic means of control over the properties of semiconductor compounds. It stimulates a detailed research on thermoelectric (TE) properties of promising TE materials depending on the degree of deviation from stoichiometry.

Bismuth telluride Bi_2Te_3 and solid solutions on its basis are well known TE materials that are widely used in the manufacture of various cooling devices and are most efficient at near-room temperatures [1-4].

Bi and *Te* components have unlimited mutual solubility in liquid state. In solid state, in *Bi-Te* system formation of a series of compounds was found (Bi_2Te_3 , Bi_7Te_3 , Bi_2Te , $BiTe$, etc.), of which only Bi_2Te_3 is melting congruently at temperature 859 K, and the rest are formed according to peritectic reactions [5, 6]. In the region of compositions between Bi_2Te_3 and Te no intermediate phases were found, and a eutectic-type state diagram takes place (eutectic temperature is 687 K). It is known that close to Bi_2Te_3 compound, maximum on liquidus and solidus curves is displaced from stoichiometric composition towards *Bi* excess, and at congruent melting point it corresponds,

according to different authors, to compositions: 59.935 at.% Te [7], 59.95 at.% Te [8] and 59.8 at.% Te [9]. To determine the boundaries of homogeneity region of Bi₂Te₃ in Bi-Te system, different authors measured charge carrier concentration $n(p)$ [10], electric conductivity σ [11], the Seebeck coefficient S [10,11], unit cell parameters [9], optical density of vapours [8], as well as the data of differential thermal analysis [9]. Today it is known that Bi₂Te₃ exists in a narrow concentration range, and the data of different authors with respect to the boundaries of homogeneity region of Bi₂Te₃ correlate rather well and correspond to 59.4–60.3 at.% Te (773-853 K) [11], 59.8-60.2 at.% Te (733-793 K) [8], 59.4-60.2 at.% Te (~850 K) [10], 59.7- 60.35 at.% Te (673 K) [9], 59.92-60.05 at.% Te (773-798 K) [7]. However, as we can see, the data available in the literature refer to sufficiently high temperatures.

Bi₂Te₃ crystallizes as tetradymite-type rhombohedral lattice based on a nine-layer packing of Bi and Te atoms (space group $R\bar{3}m-D^5_{3d}$) [2, 3, 12-14] and is characterized by anisotropy of properties. Tetradymite-type rhombohedral lattice can be considered as a hexagonal layered structure where one cell is a successive superposition of three five-layer groups with alternation of layers according to scheme:– B¹– A– B²– A– B¹–, where A – Bi, B – Te, and indexes 1 and 2 point to the difference in positions of Te atoms in crystal lattice. X-ray studies of other phases of Bi-Te system [12-14] have shown that all of them crystallize as a hexagonal layered structure consisting of five atomic packings with intercalated additional layers of one sort of atoms perpendicular to the c axis and different number and sequence of layers.

Under deviation from stoichiometry, structural defects are formed in crystal lattice. It was established that with stoichiometric composition (60 at.% Te) and under deviation from it towards Bi excess, p -type conductivity is manifested, and towards Te excess– n -type. In order to explain the abnormal behaviour of charge carriers as compared to that which occurs, for instance, in PbTe, T. Harman was the first to suppose [15] that in nonstoichiometric Bi₂Te₃ it is antisite defects that are mostly formed. In [16], for identification of the type of defects the experimentally obtained values of density of bismuth telluride single crystals of various compositions were compared to the results of theoretical calculation on the assumption of various defect formation models. It was shown that under deviation from stoichiometry towards Bi excess, formation of antisite defect Bi_{Te} is most possible, and with Te excess the experimental values of density were closer to the values calculated on the assumption of vacancy model. However, the authors of [16] indicated the proximity of theoretical calculations disregarding the composition dependence of lattice parameter and using a series of assumptions in the determination of charge carrier concentrations from the electric data. Therefore, it is generally considered that the main type of defects under deviation from stoichiometry both towards Te excess and towards Bi excess are antisite defects Te_{Bi} and Bi_{Te}, respectively.

In a number of works, the TE properties S [11, 10, 2, 17, 18], R_H [10, 2, 17, 18], $n(p)$ [10, 2, 17, 18], electric conductivity σ [11, 17, 18, 2], thermal conductivity λ [10, 17, 18], the Fermi level [18], the Lorentz number [18], TE figure of merit Z [2, 17] were studied as a function of

composition in the vicinity of Bi₂Te₃. TE properties were generally measured on single crystal samples. In the majority of works available for characterization of the degree of deviation from stoichiometry in single crystals, it is not the composition of crystals that was employed, but the composition of the melt from which crystals were grown (point on liquidus line) or the temperature of isothermal annealing (these two characteristics are interrelated), or charge carrier concentration in the obtained crystals whose composition does not coincide with the composition of the liquid phase [10, 2, 17, 18]. A direct relation between the composition of crystals and their properties can be established (as it was first done in [10]) by calculation of defect concentration on the basis of $n(p)$ values and lattice parameters, however, in this case one should know exactly the electric effect of this or other stoichiometry defect, its valence state.

The authors of [10] obtained dependences of $n(p)$, S , R_H on the composition of the melt of which Bi₂Te₃ single crystals were grown, and first showed that crystal which is in equilibrium with the liquid of composition 62.8 at.% Te has minimum concentration of charge carriers of each type, and its density coincides with the density calculated by parameters of crystal lattice of stoichiometric composition. At higher Te concentration in the melt, crystals have n -type conductivity, at lower p -type conductivity.

Similar investigations were performed in [2, 17, 18], but the authors used an advanced method of growing single crystals that allowed their quality to be enhanced. They also obtained the dependences of S , R_H , σ , λ , Z on the composition of the melt. According to this data, maximum values of TE figure of merit ($Z = 2.9 \cdot 10^{-3} \text{ K}^{-1}$) were observed for materials with electron conductivity and corresponded to melt composition 64 at.% Te.

Analysis of works available on the investigation of properties behaviour in the region of compositions in the vicinity of Bi₂Te₃ in Bi-Te system shows that the literature practically lacks information on studying the properties of polycrystals, though for TE applications mostly polycrystalline samples are used. Moreover, as long as solidus line defining ultimate solubility of Bi or Te in Bi₂Te₃ in solid state is built only for sufficiently high temperatures, and the region of application of Bi₂Te₃ based materials – close to room temperature, it is also desirable to obtain such information for lower temperatures.

The purpose of the present work is to perform a detailed study of the dependences of TE properties and microhardness on Te concentration in polycrystalline bismuth telluride exposed to a long-term isothermal annealing in solid state.

Experimental procedure

Synthesis of polycrystals was performed by direct melting of Bi and Te of high degree of purity (99.999 at. % of the basic component) in evacuated quartz ampoules at $(1020 \pm 10) \text{ K}$ for 5 – 6 hours, annealing at $(670 \pm 5) \text{ K}$ for 300 hours and subsequent cooling to room temperature at the rate of switched off furnace. Altogether, 28 alloys of different composition were prepared in

the range of concentrations 57.5 – 70 at.% Te. Some compositions (e.g. 60 at.% Te, 59.93 at.% Te, 62.8 at.% Te) were prepared 2-3 times to be sure in the reproducibility of composition and properties at resynthesis. Comparing the properties of samples of the same composition after resynthesis showed that the difference in the values of characteristics did not exceed their measurement errors.

Microhardness was measured at room temperature on PMT-3 instrument, using a diamond pyramid, at constant load on indenter $P = 0.49$ H. The time of loading, holding under load and the time of load relief made 10 s each. Adjustment of the instrument was performed by means of fresh cleavages of KCl crystals. Surface preparation for measurement of H (grinding, mechanical polishing and etching) was identical for all the samples. Measurement of H of each sample was done at least at 30 sample points with subsequent statistical treatment of the results. The relative mean-square fluctuation did not exceed 3% for all the samples.

The Seebeck coefficient S was measured by compensation method with respect to copper electrodes at room temperature at least at 20 sample points with subsequent statistical treatment of measured results. Mean-square relative error for all the samples did not exceed 3 %. The electric conductivity σ and the Hall coefficient R_H were measured by standard dc method at an accuracy of ± 5 %. The Hall mobility μ was calculated as $\mu = R_H \cdot \sigma$, and the value of thermoelectric power – by the formula $P = S^2 \cdot \sigma$. Measurements were performed on the samples shaped as parallelepipeds of size 10x2x3 mm, cut out of the obtained ingots.

Results

Figs. 1, *a-e* show dependences of S , R_H , μ , H and P on Te concentration. It can be seen that these dependences are of sufficiently complicated non-monotonic nature.

S and R_H dependences (Fig. 1, *a, b*) are much alike: on both curves at stoichiometric composition (60 at.% Te) with hole conductivity there are maxima, under deviation from stoichiometry towards tellurium, S and R_H are reduced, and in the vicinity of composition 61 at.% Te there is inversion of conductivity type $p \rightarrow n$. Note that position of the inversion point is very close to that determined in [11], where S and σ were measured in the vicinity of stoichiometric composition on polycrystalline samples. In the region with n -type conductivity, S increases to ~ 64 at.% Te, following which it practically does not change. The composition dependence of R_H in n -region is more complicated: after the inversion point R_H increases, passes through maximum at ~ 63 at.% Te, reduces to 65 at.% Te, keeping later practically constant value.

On the composition dependence of μ (Fig. 1, *c*) there are two distinct maxima: at stoichiometric composition (60 at.% Te) in p -region and at composition ~ 63 at.% Te in n -region.

The concentration dependence of H is of unusual nature H (Fig. 1, *d*). Under deviation from stoichiometric composition either side (to ~ 59.5 and 61 at.% Te), H increases, which agrees with generally observed strengthening of crystal lattice on introduction of defects into crystal.

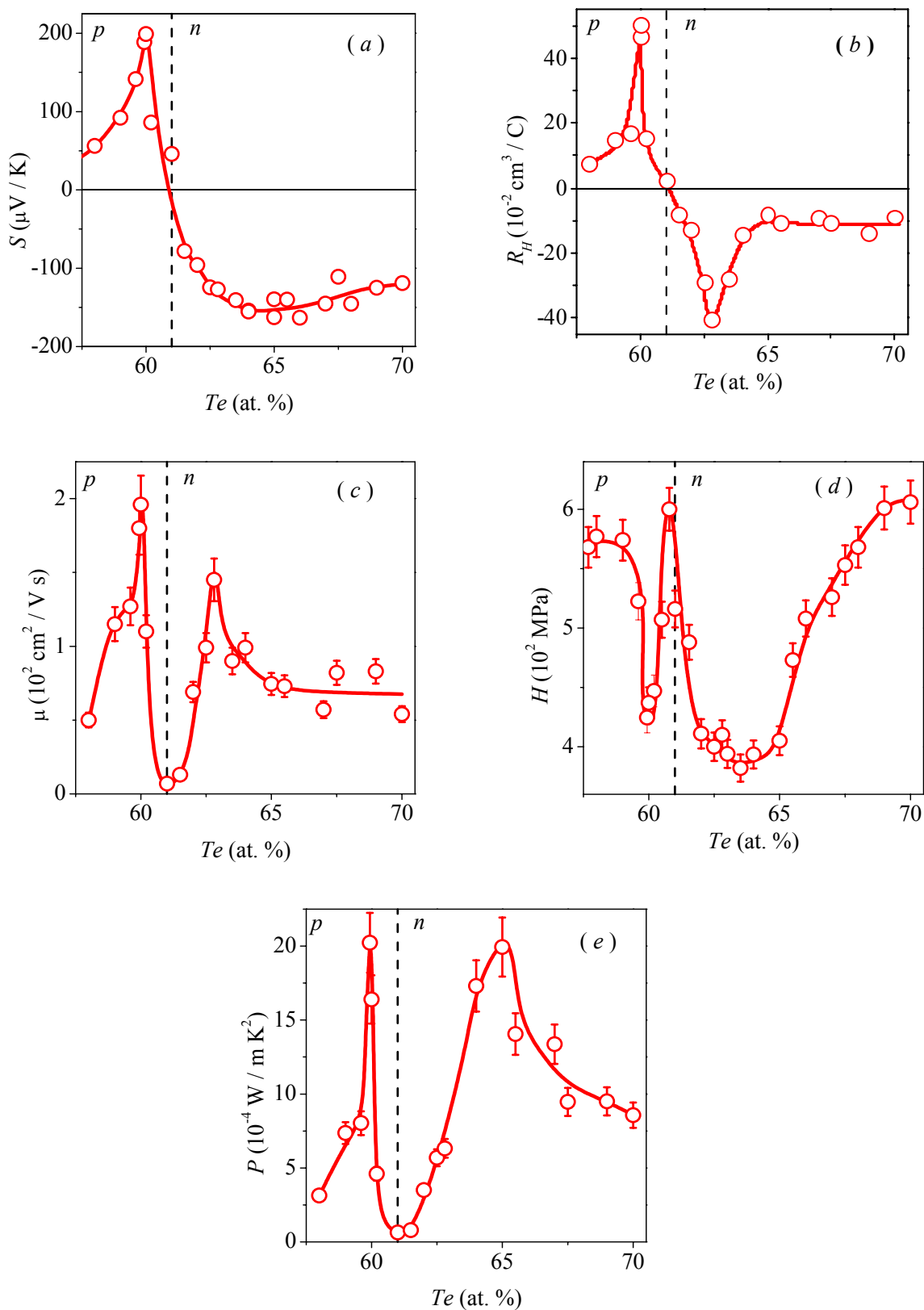


Fig. 1. Dependences of the Seebeck coefficient S (a), the Hall coefficient R_H (b), charge carrier mobility μ (c), microhardness H (d) and thermoelectric power $P = S^2\sigma$ (e) on Te concentration in $\text{Bi} - \text{Te}$ system with compositions in the vicinity of Bi_2Te_3 .

However, at 61 at.% *Te* there is a drastic drop of *H* to the values even lower than at 60 at.% *Te* which continues to ~ 63 at.% *Te*. As a result, the compositions 60 and 63 at.% *Te* are matched by minima of *H*, the inversion point of conductivity sign is matched by maximum of *H*. Then *H* is monotonically increased with growth of *Te* concentration to 70 at.% *Te*. A drastic reduction of *H* observed in the range of compositions 61-63 at.% *Te*, is accompanied by growth of σ , μ , R_H and *S*. Close to 63 at.% *Te* on the dependences of σ , μ , R_H there are maxima, on *H* – composition curve – minimum, and the Seebeck coefficient practically ceases changing. Thermoelectric power shows two maxima on the dependence of *P* on *Te* concentration – at 60 and ~65 at.% *Te*.

Discussion of the results

Deviation from stoichiometric composition of compound results in formation of structural defects, which, in turn, should lead to charge carrier concentration growth (if defects are electrically active), increase in scattering of electrons (holes) and phonons on defects, as well as growth of crystal lattice stresses. Hence, it is not difficult to explain the observed drop in *S*, R_H and μ , as well as growth of *H* under deviation from stoichiometric composition either side. The appearance of electrically active antisite defects of this or other type under deviation from stoichiometry leads to growth of charge carrier concentration, hence, to reduction of *S* and R_H , and increase of defect scattering – to drop of μ . As long as introduction to stoichiometric compound of various defects, including nonstoichiometry defects, leads to lattice strengthening and growth of *H*, increase of *H* under deviation from stoichiometry to ~ 61 and 59.5 at.% *Te* (Fig. 1, *d*) can approximately indicate the boundaries of *Bi*₂*Te*₃ homogeneity region. On the side of *Bi* excess, the boundaries of homogeneity region can be determined accurately enough by the position of a bend on the composition dependence of *H*.

The situation is more difficult with determination of the boundary of *Bi*₂*Te*₃ homogeneity region on the side of *Te* excess. In conformity with the state diagram of *Bi-Te*, with *Te* excess with respect to stoichiometric composition and cooling of the melt below eutectic temperature under conditions of thermodynamic equilibrium, the alloys are a two-phase mixture of solid solution based on *Bi*₂*Te*₃ and *Te*. It can be assumed that after a long-term isothermal annealing that we performed at 670 K the equilibrium at this temperature is reached. Subsequent cooling at the rate of switched off furnace to room temperature, with regard to low diffusion rate at such low temperatures and low exposure time, will hardly change the situation and one can presumably speak about keeping of equilibrium at 670 K on cooling to room temperature.

As mentioned above, the dimensions of *Bi*₂*Te*₃ homogeneity region at elevated temperatures, according to different authors, do not exceed the range of compositions 50.4 - 60.5 at.% *Te*. It was also informed [2, 17] that with lowering of temperature the limit solubility of *Te* is increased. Though we were dealing with high temperatures, it can be assumed that expansion of homogeneity region occurs up to eutectic temperature (687 K), and at 670 K (annealing temperature) close to eutectic temperature, the boundary of homogeneity region on the side of *Te*

excess exceeds 61 at.% Te . The fact that a change in conductivity sign takes place at 61 at.% Te shows that this composition is within homogeneity region, though close to its boundary, as testified by the observed growth of H only to ~ 61 at.% Te .

On the other hand, the fact that the inversion point corresponds to 61 at.% Te , rather than to stoichiometric composition, which might be expected with regard to the data obtained in [10, 17] for monocrystalline samples requires explanation. This can be due to several factors. First, displacement of congruent melting point towards Bi excess [7-9] leads to the fact that stoichiometric composition already comprises sufficiently high concentration of p -type charge carriers as a result of appearance of antisite defect Bi_{Te} . Therefore, under deviation from stoichiometry towards Te excess and the emergence of donor type defects (antisite defect Te_{Bi}) a certain number of the latter is needed in order to neutralize the acceptor effect of antisite defects present in stoichiometric Bi_2Te_3 , which results in displacement of the inversion point towards Te . Moreover, as mentioned above, under deviation from stoichiometry towards Te excess, formation of antisite defects Te_{Bi} is most probable, however, according to [9], it is not impossible that Bi cation vacancies will be formed that demonstrate an acceptor effect. In this case the inversion point will be further displaced towards tellurium excess.

Assuming that the limit solubility on the side of Te is close to 61.0 at.% Te , it is not clear why after ~ 61 at.% Te H drastically drops, reaching the value which proves to be lower than the value of H for stoichiometric Bi_2Te_3 (Fig. 1, *d*). It points to a drastic reduction of crystal lattice distortions, crystal weakening and can testify to the presence of a phase transition. This is also in agreement with mobility growth accompanying a drop in H (Fig. 1, *c*).

In some works of the present author with co-authors there were revealed concentration anomalies of various physical properties, including H and μ , in the region of low impurity concentrations (0.5–1.0 at.%) that were attributable to critical phenomena attending phase transition of percolation type from dilute to concentrated solid solutions [19]. It was suggested that any solid solution has weakening area corresponding to transition to state when interaction of defects covers the entire crystal, leading to qualitative change in the dynamic motion of dislocations, their mobility increase, the macroscopic consequence of which is weakening, i.e. drop in H . Obviously, said weakening effect should be particularly significant with the ordered arrangement of defects. In this connection, it may be assumed that in the vicinity of homogeneity region boundary the concentration of defects becomes so considerable that percolation channels are formed connecting deformation fields of separate defects and piercing crystal. Attainment of percolation threshold stimulates self-organization processes in defects subsystem reducing crystal internal energy and leading to formation of a new (in addition to Bi_2Te_3) ordered phase having its own stoichiometry and homogeneity region. Therefore, properties keep changing with composition.

Another reason for a complicated composition dependence of properties can be effects attending second phase precipitations in passing through solidus line. In conformity with Bi-Te

diagram of state, on reaching the boundary of homogeneity region there must start *Te* precipitation. *Te* crystal lattice cannot be obtained by simple redistribution of atoms in the sites of *Bi₂Te₃* lattice for the distances commensurate with interatomic distances, as in case of ordering, since *Bi₂Te₃* and *Te* structures are essentially different. Therefore, second phase precipitation can be preceded by formation of intermediate nonequilibrium structures. In this case, properties can also change in a complicated fashion. Assuming that after 61 at.% *Te* second phase precipitations did start, one can hardly expect in this case a drastic drop in *H*, since at the initial step second phase precipitations are generally fine dispersed, crystal lattice is strengthened and *H* increases, rather than drops.

It can be further supposed that the observed effects are in a certain way related to the impact of kinetic factors. On cooling of alloys from eutectic to room temperatures, in conformity with the equilibrium state diagram the homogeneity region must narrow. On considerably quick cooling of alloys at a rate of switched off furnace from annealing (670 K) to room temperature, because of low diffusion rate of atoms at these temperatures and short exposure time, this process is not realized completely, but a certain intermediate nonequilibrium state is created whereby crystal is oversaturated with defects. However, on introduction of additional number of excess *Te*, the system jumps into equilibrium (or quasi-equilibrium) state, leading to a drastic reduction of *H* and growth of μ . With further concentration increase of superstoichiometric *Te*, the systems comes to equilibrium state and electrophysical properties cease to change with composition, as it should be in two-phase system. With solid solution decomposition in a quasibinary system in equilibrium state the properties of matrix phase should not change with composition. The growth of *H* in eutectic region 65-70 at.% *Te* is due to the fact that we measure averaged *H* value which increases due to concentration growth of *Te* whose microhardness exceeds *H* of *Bi₂Te₃*.

Thus, possible reasons for the observed change in TE parameters up to ~ 65 at.% *Te* include: 1) formation of intermediate ordered phase with its own stoichiometry and homogeneity region similar to the way in which it occurs on the side of *Bi* excess; 2) complicated process of the onset of second phase precipitation and possible formation of intermediate nonequilibrium states; 3) impact of kinetic factors – the appearance of nonequilibrium states in which the alloys are found after quick cooling from a long-term annealing to room temperature, and gradual transition to equilibrium with increasing degree of deviation from stoichiometry.

Final identification of the reasons for complicated dependence of TE and mechanical properties of *Bi₂Te₃* on the degree of deviation from stoichiometry toward *Te* excess calls for thorough investigation of microstructure and crystal structure depending on the composition and thermal treatment, which will be the subject of our future studies.

Conclusions

The effect of deviation from stoichiometry on thermoelectric and mechanical properties of *Bi₂Te₃* semiconductor compound with a change in *Te* content from 57.5 to 70 at.% was studied at

room temperature on polycrystalline samples subject to a long-term homogenizing annealing at 670 K and subsequent cooling at a rate of switched off furnace. A set of experimental studies performed and their analysis allowed making the following conclusions.

After the employed technique of samples preparation the boundaries of homogeneity region are within 59.5 – 61 at.% *Te*. In this region, under deviation from stoichiometric composition (60 at.% *Te*) both toward *Bi* excess and toward *Te* excess there is a drop in *S*, *R_H* and μ and growth of *H*, which is attributable to introduction to crystal of nonstoichiometry defects increasing charge carrier concentration and the level of stresses in crystal lattice. With increase in *Te* concentration, in the vicinity of 61 at.% *Te* there is inversion of conductivity type $p \rightarrow n$.

A complicated character of properties change with composition beyond the homogeneity region in electron conductivity area is revealed. Close to 63 at.% *Te* on the composition dependences of properties there are extremes, and starting from ~ 65 at.% *Te*, *S*, *R_H* and μ practically do not change with composition, and *H* is monotonically increased.

Among possible reasons for the observed complicated nature of properties change beyond the homogeneity region are: 1) formation of intermediate ordered phase with its own stoichiometry and homogeneity region after percolation threshold is reached in defects subsystem; 2) complicated process of the onset of second phase precipitation (*Te*) and possible formation of intermediate nonequilibrium states; 3) impact of kinetic factors – the appearance of metastable states in which the alloys are found after quick cooling from annealing to room temperature, and gradual transition to equilibrium with increasing degree of deviation from stoichiometry.

Maximum values of thermoelectric power *P* correspond to stoichiometric composition and 65 at.% *Te*.

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