

Effect of Deviation from Stoichiometry on Thermoelectric Properties of Bi₂Te₃ Polycrystals and Thin Films in the Temperature Range 77-300 K

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Bi₂Te₃ semiconductor compound and Bi₂Te₃-based solid solutions are presently among the best low-temperature thermoelectric materials. One of the methods of controlling the conductivity type and properties of Bi₂Te₃ is changing the stoichiometry of this compound. Earlier, we have obtained the room-temperature dependences of mechanical and thermoelectric properties of Bi₂Te₃ polycrystals on the degree of deviation from stoichiometry. The goal of this work is to investigate the behavior of such dependences at other temperatures. Bismuth telluride polycrystals with compositions in the range of 59.6-67.5 at. % Te were obtained, and for all the crystals the Seebeck coefficient, the Hall coefficient, electrical conductivity and charge carrier mobility were measured in the temperature range 77-300 K. On the basis of the temperature dependences, the isotherms of kinetic coefficients were plotted. It was found that similar to the room-temperature isotherms, the isotherms at lower temperatures were non-monotonic: they exhibited inversion of the conductivity sign between 60.5 and 61.0 at. % Te and extrema near 60.0 and 63.0 at. % Te. The experimental data are interpreted taking into account changes in the band and defect structures of Bi₂Te₃ under varying stoichiometry. The obtained results make it possible to control thermoelectric properties of Bi₂Te₃ polycrystals in the temperature range 77-300 K by changing the degree of deviation from stoichiometry.

Keywords: Bi₂Te₃, Stoichiometry, Electrical conductivity, Seebeck coefficient, Hall coefficient, Charge carrier mobility, Temperature dependences.

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1. INTRODUCTION

Bi₂Te₃ semiconductor compound and Bi₂Te₃-based solid solutions are well-known thermoelectric (TE) materials, widely used in the production of various kinds of cooling devices and most efficiently operating near room temperature [1-4]. Recently, interest in studying Bi₂Te₃ crystals and thin films has grown sharply due to the prediction and subsequent experimental evidence of their exhibiting special properties, characteristic of 3D-topological insulators [5-7]. In recent years, many works have appeared in which the possibility of using the properties of topological insulators in thermoelectricity was suggested [8-10].

Bi₂Te₃ crystallizes in a layered rhombohedral structure with five-layer packets perpendicular to the third-order symmetry axis. A characteristic feature of Bi₂Te₃ single crystals is a pronounced anisotropy of properties. To explain the strong anisotropy, a Fermi six-ellipsoid surface model for the valence and conduction bands with the centers of ellipsoids on the symmetry planes was proposed, and to date, this model best describes experimental data. Some authors suggest the presence of two subbands both in the conduction band and in the valence band [1-3, 11-14].

In a number of works, the temperature dependences of transport coefficients of Bi₂Te₃ [1-4] were studied. It was established that at the temperatures close to room temperature, scattering by acoustic phonons prevails even in heavily doped samples with charge carrier concentrations up to $\sim 10^{-19} \text{ cm}^{-3}$. In some works, the contribution of scattering by optical phonons as well as the existence of a weak dependence of the effective mass m^* on temperature $m^* \sim T^x$ is assumed. The values of the

exponents ν in the temperature dependences of charge carrier mobility μ_H for n - and p -Bi₂Te₃ crystals were in the range $\nu = 1.5-2.0$ [1-3]. Intrinsic conductivity starts to manifest near room temperature. In most works, only p - and n -Bi₂Te₃ single crystals were studied, and there is far less information in the literature on the properties of polycrystals, although, it is polycrystals that are mainly used for TE applications.

It is known [1-3] that Bi₂Te₃ has a narrow homogeneity region in the Bi-Te system and, depending on the character of the deviation from stoichiometry, can exhibit either p - or n -type conductivity. Under deviation from stoichiometry, structural defects are formed in the crystal lattice. It is usually considered that the main type of defects in the case of deviation from stoichiometry both towards an excess of Te and towards an excess of Bi are antisite defects Te_{Bi} and Bi_{Te}, respectively. The stoichiometric Bi₂Te₃ (60.0 at. % Te) exhibits p -type conductivity due to the shift of the maximum in the liquidus and solidus curves to the Bi-rich side and the presence of antisite Bi_{Te} defects. One of the methods of controlling the conductivity type and properties of Bi₂Te₃ is changing the stoichiometry of this compound.

Despite the large number of works dealing with the kinetic properties of both stoichiometric Bi₂Te₃ and Bi₂Te₃ with impurities [1-4], there are significantly fewer studies on the effect of deviation from stoichiometry on the TE phenomena in this material. In the available works, only single crystals were studied, besides the authors did not measure the dependences of the TE properties on the stoichiometry at different temperatures.

The authors of [15] conducted a detailed study of the room-temperature dependences of microhardness and TE properties on Te concentration in the Bi-Te system near

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the stoichiometric composition Bi_2Te_3 (60 at. % Te). In [15], polycrystalline samples subjected to long-term homogenizing annealing at 670 K and slowly cooled after annealing to room temperature were investigated. It was found that after such heat treatment, the concentration dependences of the Seebeck coefficient S , the Hall coefficient R_H , electrical conductivity σ , and μ_H were clearly non-monotonic. In particular, under the deviation from the stoichiometric composition both to the Bi-rich side and to the Te-rich side, S , R_H , and μ_H decrease; near ~ 61 at. % Te the inversion of the conductivity type $p \rightarrow n$ occurs and the minimum values of σ and μ_H are observed; in the vicinity of 63 at. % Te extrema are observed and starting from ~ 65 at. % Te, S , R_H and μ_H practically do not change with the composition. It was shown that the composition of crystals with different stoichiometry and type of conductivity is fairly well reproduced in films obtained by thermal evaporation in vacuum of these crystals [16-18].

Since Bi_2Te_3 belongs to the low-temperature TE materials, it is necessary to know how deviation from stoichiometry affects properties not only at room temperature but also at lower temperatures. Besides, it is important to obtain such information for polycrystals.

The main purpose of this work was to measure the temperature dependences of TE properties in the range 77-300 K for Bi_2Te_3 polycrystals with different stoichiometry and based on these dependences to plot the isotherms of the properties.

As a result of the study, it was shown that the behavior of the isotherms of TE properties in the studied temperature range practically corresponds to the behavior of the room-temperature isotherms obtained in [15]. It also follows from the results that the character of the temperature dependences of S , R_H , σ , and μ_H is similar to that observed for single crystals.

2. EXPERIMENTAL

The objects of the study were bismuth telluride polycrystals with different degrees of deviation from stoichiometry within the range of compositions (59.6-67.5 at. % Te). The samples were synthesized by the fusing of high purity (99.999 at. % of the main component) Bi and Te in evacuated quartz ampoules at 1020 ± 10 K, subsequent annealing at 670 ± 5 K for 300 hours and cooling to room temperature in the turned off furnace. Using polycrystals with 60.0 and 62.8 at. % Te as initial materials, we prepared films with thicknesses $d = 620$ and 325 nm respectively by thermal evaporation in vacuum onto glass substrates. For each sample, transport coefficients were measured in the temperature range 77-300 K. R_H and σ were determined using a conventional dc method and a magnetic field of 0.8 T. The samples were placed in liquid nitrogen and the temperature dependences were measured during the subsequent heating of the samples to room temperature at an average rate of 1 degree per minute. The measurements were carried out on parallelepiped-shaped samples with dimensions of $10 \times 2 \times 3$ mm³, cut from the obtained ingots. Six ohmic contacts were soldered with indium to the sample surface. The error in the R_H and σ measurements did not exceed ± 5 %. S was measured by compensation probe method relative to Cu

electrodes with an accuracy of ± 3 %. The temperature gradient ΔT in the measurements of S was 2 K. Based on the obtained values of R_H and σ , the Hall charge carrier mobility was calculated as $\mu_H = \sigma R_H$. The TE power factor P was determined using the equation $P = S^2 \cdot \sigma$.

3. RESULTS AND DISCUSSION

The results of measurements of S and R_H showed that in the entire temperature range studied in this work, the samples with Te concentrations less than ~ 60.8 at. % Te exhibit p -type conductivity, and samples with higher Te concentration exhibit n -type conductivity, which is consistent with the available literature data [1-3, 7-16]. Concentrations of both electrons (n) and holes (p) were estimated using R_H values at $n(p) \sim 10^{19}$ cm⁻³, indicating a strong degeneracy of electron and hole gases. Due to the high dielectric constant of Bi_2Te_3 , degeneracy is observed already at charge carrier concentrations $\sim 10^{17}$ cm³ [3].

3.1 Polycrystals with p -type Conductivity

In Fig. 1, the temperature dependences of σ , R_H , and μ_H for the samples with different Te content (59.6, 60.0 and 60.5 at. % Te) exhibiting p -type conductivity are presented. It is seen that for all samples, σ and μ_H decrease with increasing temperature, which confirms degeneracy of the hole gas.

It is also seen in Fig. 1 that with increasing temperature, the values of R_H for all compositions increase ~ 1.5 -2 times in the range of 77-300 K, not remaining constant despite strong degeneracy.

As noted above, the stoichiometric Bi_2Te_3 due to the shift of the maxima in the solidus and liquidus curves in the Bi-Te system relative to the stoichiometric composition to the Bi-rich side, contains Bi_{Te} antisite defects, and that is why exhibits p -type conductivity. Using a one-band model approximation and taking into account a strong degeneracy of the hole gas, which assumes that R_H does not depend on temperature, it is difficult to explain the increase in R_H with temperature. The observed tendency for R_H to increase with increasing temperature (Fig. 1) may indicate a decrease in the concentration of p -type charge carriers, i.e. a decrease in the number of electrically active p -type defects with temperature.

Under deviation from stoichiometry in the direction of excess Bi (59.6 at. % Te), the concentration of Bi_{Te} antisite p -type defects should increase (if the indicated composition is within the Bi_2Te_3 homogeneity region and Bi_{Te} antisite defects remain the prevailing type of defects) or at least remain constant (outside the homogeneity region). In both cases the degree of degeneracy should not decrease, and the increase in R_H with temperature also requires explanation.

One can suggest that at low temperatures, apart from Bi_{Te} antisite defects, other p -type defects are formed and their concentration decreases with increasing temperature. The presence of a step in the $R_H(T)$ curve for the sample containing 59.6 at. % Te in the temperature range of 150-200 K (Fig. 1a) indicates the possibility of the existence of two types of such defects.

Some authors observed an increase in R_H with increasing temperature in the range 77-300 K for p - Bi_2Te_3 single crystals and attributed it to the existence of an

additional subband in the valence band with high effective mass and low charge carrier mobility [3]. With increasing temperature and changing location of the Fermi level in the valence band, the relative contribution of “light” and “heavy” holes to the kinetic coefficients changes, thus leading to an increase in R_H with temperature.

It is also suggested that the increase in R_H with temperature in p - Bi_2Te_3 may be associated with the change in the degree of the degeneracy of hole gas or the change in the mechanism of charge carrier scattering with changing temperature [3].

One should also take into account possible effect of kinetic factors. When the compositions of alloys are close to the inversion point, the defect structure and properties of a system become very sensitive to changes in composition, temperature, heat treatment and other factors. The probability of the realization of various non-equilibrium states and, accordingly, formation of non-equilibrium defects increases. Taking this into consideration, one can suggest that due to sufficiently rapid cooling of the samples immersed in liquid nitrogen, they become over-saturated with defects, whose concentration exceeds the equilibrium concentration. Under heating of such non-equilibrium system, due to an increase in the diffusion rate, which leads to the movement and partial annihilation of defects, complex processes can take place. These processes are caused by the relaxation of the system towards an equilibrium state. As a result, the behavior of the $R_H(T)$ dependences becomes more complex. Obviously, the higher the diffusion rate, the lower the probability of non-equilibrium state occurrence.

In Fig. 2a, the $R_H(T)$ dependences for a p - Bi_2Te_3 polycrystal with the stoichiometric composition and a 620 nm thick film prepared from this polycrystal are presented. One can see that the increase in R_H with temperature is observed for the crystal only, which can indicate that since the diffusion rate in thin films is higher, the probability of the occurrence of non-equilibrium states decreases. Another reason could be that in contrast to a polycrystal, a film has a certain orientation [18]. However, as an increase in R_H with temperature is observed in single crystals too [3, 14, 15], apparently, orientation does not account for the increase in R_H under increasing temperature.

One should also take into account that grain boundaries in polycrystals are defects that can make a substantial contribution in kinetic coefficients, and their contribution can depend on temperature, because under increasing temperature, the mechanism of charge carrier scattering can change, for example, from predominant scattering by impurities (defects) to predominant scattering by phonons. However, as an increase in R_H with increasing temperature was observed by a number of authors in single crystals as well, the presence of grain boundaries and other defects cannot be a determinant factor.

If the assumption about a two-band model of valence band is true, it remains unclear why an increase in R_H is not observed in thin films under increasing temperature (see Fig. 2a).

Under deviation from stoichiometry in the direction of excess Te, along with Bi_{Te} antisite defects that are

present in the stoichiometric Bi_2Te_3 , Te_{Bi} antisite defects may appear. As a result, there are at least two types of defects (Bi_{Te} and Te_{Bi} antisite defects) in the crystal, and, accordingly, two types of charge carriers (electrons and holes) with different effective masses and mobilities. With increasing Te concentration, the contribution of n -type Te_{Bi} defects increases as compared to that of p -type Bi_{Te} defects, the compensation of the charge of holes by emerging electrons takes place, R_H decreases and at a certain composition close to 60.8 at. % Te, the inversion of the conductivity sign occurs. If there are several types of charge carriers, it is impossible to calculate charge carrier concentration using the equation for a single type of carriers, and low values of R_H do not necessarily indicate a high concentration of charge carriers.

Plotting the $\mu_H(T)$ dependences in double logarithmic coordinates, we determined exponents ν in the temperature dependences of charge carrier mobility $\mu_H \sim T^\nu$ (Fig. 3). It is seen that the value of ν observed for the stoichiometric composition of Bi_2Te_3 ($\nu = -1.5$) is in good agreement with the results of a number of studies on the

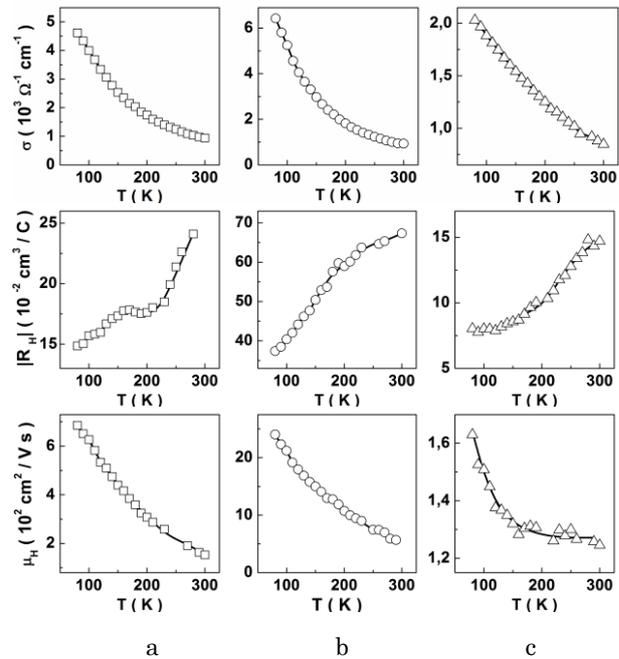


Fig. 1 – Temperature dependences of electrical conductivity σ , the Hall coefficient R_H , and Hall charge carrier mobility μ_H for polycrystalline p - Bi_2Te_3 samples with 59.6 (a), 60.0 (b) and 60.5 (c) at. % Te

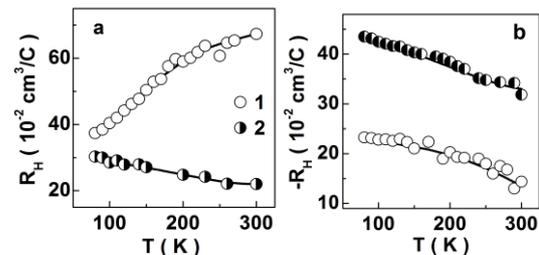


Fig. 2 – Temperature dependences of the Hall coefficient R_H for p - Bi_2Te_3 thin film ($d = 620$ nm) (a) and n - Bi_2Te_3 thin film ($d = 325$ nm) (b) grown from polycrystals with 60.0 (a) and 62.8 at. % Te (b): 1 – bulk crystal; 2 – film

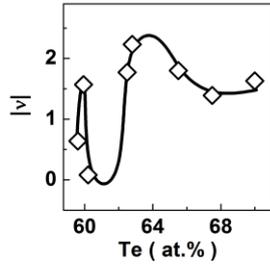


Fig. 3 – The dependence of the exponent ν in the temperature dependence of the Hall charge carrier mobility $\mu_H \sim T^\nu$ on the Te concentration in the Bi-Te system near Bi_2Te_3 stoichiometric composition

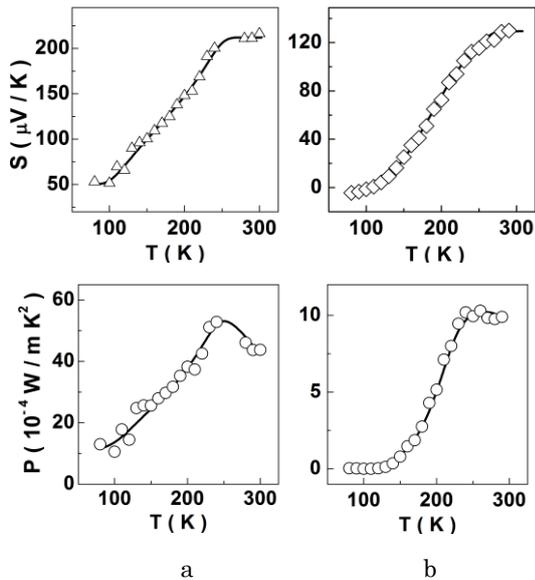


Fig. 4 – Temperature dependences of the Seebeck coefficient S and thermoelectric power factor $P = S^2 \sigma$ for polycrystalline $p\text{-Bi}_2\text{Te}_3$ samples with 59.6 (a) and 60.5 (b) at. % Te

temperature dependences of kinetic properties of Bi_2Te_3 [1-4] and corresponds to scattering by acoustic phonons.

It is also seen in Fig. 3 that deviation from the stoichiometric composition both to the Bi-rich side (59.6 at. % Te) and to the Te-rich side (60.2 at. % Te) leads to a decrease in the exponent ν , which can be attributed to an increase in the contribution of impurity scattering when defects are introduced in the stoichiometric Bi_2Te_3 .

In Fig. 4, the temperature dependences of the Seebeck coefficient and thermoelectric power factor $P = S^2 \sigma$ for p -type samples are shown. It can be seen that S increases with temperature up to ~ 250 K, and then practically does not change. Such character of the $S(T)$ dependence is consistent with the results of other authors obtained for single crystals and explained by the appearance of intrinsic conductivity [1-4]. From the $P(T)$ dependences it is seen that P increases up to ~ 250 K and then decreases (Fig. 4). The maximum values of both S and P are attained at ~ 250 K.

3.2 Polycrystals with n -type Conductivity

In Fig. 5, the temperature dependences of σ , R_H , and μ_H for the alloys of the Bi-Te system with n -type

conductivity and with different Te concentrations (62.8, 65.0, 67.5 at. %) are presented. As seen, like in the case of the samples exhibiting p -type conductivity, σ and μ_H decrease with increasing temperature, which is indicative of the degeneracy of the electron gas. One can observe that up to $T \sim 200$ K R_H does not depend on temperature, which is characteristic of degenerate semiconductors, and then decreases, indicating that the region of intrinsic conductivity is approached. Since the compositions are rather far from the inversion point (~ 60.8 at. % Te), one type of charge carriers (electrons) prevails. By constructing the $\mu_H(T)$ dependences in double logarithmic coordinates, the exponents ν in the temperature dependences of μ_H for the alloys exhibiting n -type conductivity were estimated (Fig. 3).

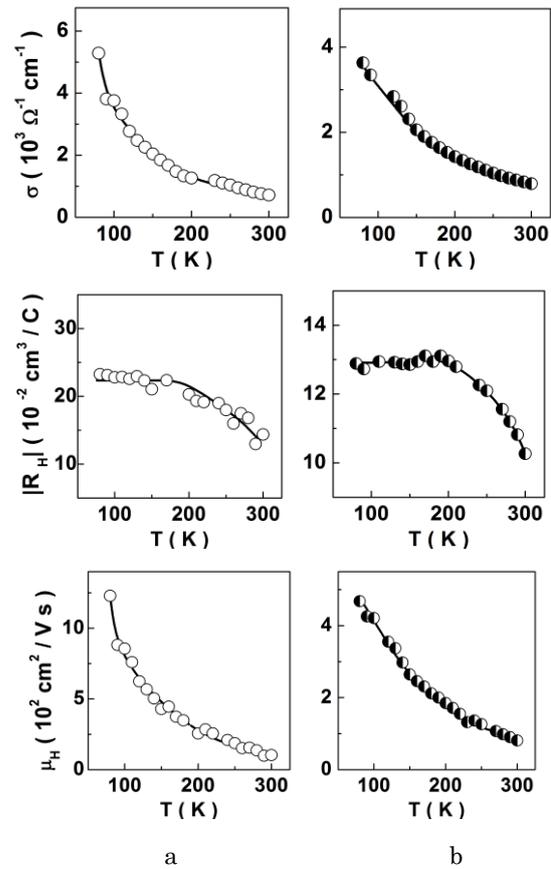


Fig. 5 – Temperature dependences of electrical conductivity σ (a), the Hall coefficient R_H (b), and Hall charge carrier mobility μ_H for polycrystalline $n\text{-Bi}_2\text{Te}_3$ samples with 62.8 (a) and 65.0 (b) at. % Te

It can be seen from Fig. 3 that 1) in the studied range of compositions (59.6-67.5 at. % Te), the maximum absolute values of ν correspond to the compositions ~ 60.0 ($\nu = -1.5$) and ~ 62.8 at. % Te ($\nu = -2.3$); 2) absolute values of ν in the n -region exceed those in the p -region. That is why it can be assumed that the mechanism of charge carrier scattering in alloys exhibiting electronic conductivity is influenced by some additional factors (besides scattering by acoustic phonons), for example, a concentration dependence of effective mass.

In Fig. 6, the temperature dependences of S and P are presented. It can be seen that like in the case of p -type

samples, S and P increase with increasing temperature up to ~ 250 K, after which S stops changing and P starts to decrease.

On the basis of the temperature dependences of the kinetic coefficients, the isotherms were drawn. Fig. 7 shows the isotherms of R_H , μ_H , S , and $P = S^2 \cdot \sigma$ at 77 and 250 K. The insets in the figures show isotherms obtained in [15] at 300 K. It can be seen that the behavior of these isotherms is similar, first, to the behavior of the dependences of R_H , μ_H , S , and P on the Te content at room temperature [15], and, second, to the behavior of the dependence of the exponent ν on the Te concentration (Fig. 3).

In the region corresponding to the electron conductivity, in the vicinity of 63 at. % Te, extrema in the property-composition dependences are observed. The authors of [15] explain the unusual behavior of the isotherms, and first of all, the increase in μ_H up to ~ 63 at. % Te, by 1) the formation of an intermediate ordered phase with its own stoichiometry and homogeneity region near the composition 62.8 at.% Te; 2) a complex process corresponding to the beginning of the separation of a second phase and the possibility of the formation of intermediate non-equilibrium states.

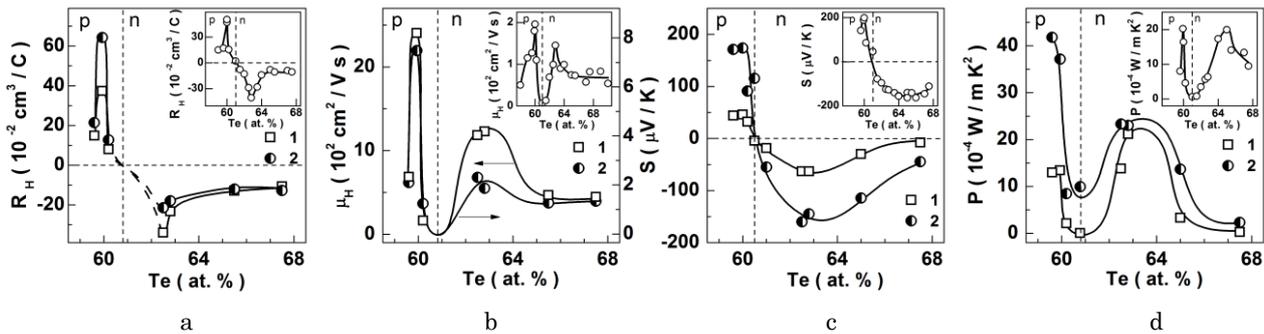


Fig. 7 – Dependences of the Hall coefficient R_H (a), the Hall charge carrier mobility μ_H (b), the Seebeck coefficient S (c), and thermoelectric power factor $P = S^2 \cdot \sigma$ (d) on Te concentration in the Bi-Te system near the stoichiometric composition at different temperatures: 1 – 80 K, 2 – 250 K. The insets show corresponding dependences at room temperature [17]

4. CONCLUSIONS

1. Charge carrier concentrations ($\sim 10^{19} \text{ cm}^{-3}$) and the behavior of the temperature dependences (77-300 K) of charge carrier mobility μ_H and electrical conductivity σ obtained for Bi_2Te_3 polycrystals with different Te concentrations (59.6-67.5 at. % Te) indicate the degeneracy of the electron and hole gases.

2. As follows from the results of measurements of the Hall coefficient and the Seebeck coefficient, in the concentration range 60.5-60.8 at. % Te, an inversion of the conductivity type from p (at Te concentrations less than ~ 60.5 -60.8 at. %) to n occurs, which is consistent with what was observed by other authors for the Bi_2Te_3 single crystals [1-4].

3. Although the hole gas in the p -type samples studied in this work is degenerate, the Hall coefficient increases with increasing temperature. The possible reasons of the observed effect include: 1) the presence of the second subband in the valence band, whose contribution to the kinetic coefficients increases with increasing temperature, 2) the change in the degree of degeneracy of the hole gas with changing temperature,

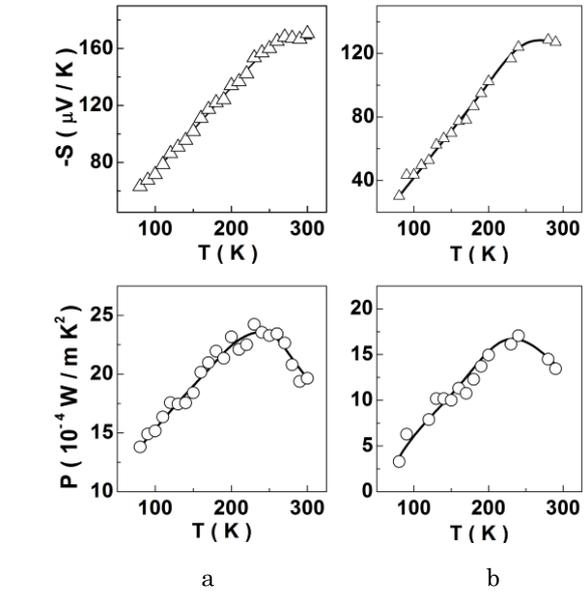


Fig. 6 – Temperature dependences of the Seebeck coefficient S and thermoelectric power factor $P = S^2 \cdot \sigma$ for polycrystalline $n\text{-Bi}_2\text{Te}_3$ samples with 62.8 (a) and 65.0 (b) The isotherms of thermoelectric properties

3) the change in the mechanism of charge carrier scattering, 4) the effect of kinetic factors, to which the system is especially sensitive in the region of concentrations close to the point of conductivity sign inversion when the system is in an unstable state.

4. An anomalous increase in the Hall coefficient with temperature is not observed for the polycrystalline samples exhibiting electron conductivity.

5. In the isotherms of S , R_H , μ_H , and the exponent in the dependence $\mu_H \sim T^\nu$ plotted on the basis of the temperature dependences (77-300 K) of the transport coefficients, extrema are observed at 60.0 and near 63.0 at. % Te. The behavior of the isotherms is similar to that of the room-temperature isotherms obtained in [15].

6. The maximum values of thermoelectric power factor $P = S^2 \cdot \sigma$ are observed at ~ 250 K and correspond to the Te concentrations 60.0 at.% Te (p -type polycrystals) and ~ 63.0 at. % Te (n -type polycrystals).

7. The obtained experimental results make it possible to control the Te properties of the Bi_2Te_3 polycrystals in the temperature range 77-300 K by varying the degree of deviation from stoichiometry.

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Вплив відхилення від стехіометрії на термоелектричні властивості полікристалів і тонких плівок Bi₂Te₃ в температурному інтервалі 77-300 К

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Напівпровідникова сполука Bi₂Te₃ та тверді розчини на її основі на цей час відносяться до числа найкращих низькотемпературних термоелектричних матеріалів. Одним із методів керування типом провідності та властивостями Bi₂Te₃ є зміна стехіометрії. Раніше ми одержали залежності механічних та термоелектричних властивостей полікристалів Bi₂Te₃ від ступеня відхилення від стехіометрії при кімнатній температурі. Мета цієї роботи – дослідження характеру цих залежностей при інших температурах. Було одержано полікристали телуриду вісмуту із складами в інтервалі 59,6-67,5 ат. % Te, і для всіх кристалів було проведено вимірювання коефіцієнта Зеебека, коефіцієнта Холла, електропровідності та рухливості носіїв заряду у температурному інтервалі 77-300 К. На основі температурних залежностей було побудовано ізотерми кінетичних коефіцієнтів. Було встановлено, що подібно ізотермам при кімнатній температурі ізотерми при більш низьких температурах мають немонотонний характер: між 60,5 і 61,0 має місце інверсія типу провідності, а поблизу 60.0 і 63 ат. % Te спостерігаються екстремуми. Дана інтерпретація експериментальних даних з урахуванням змін у зонній та дефектній структурі Bi₂Te₃ при зміні стехіометрії. Одержані результати дають можливість керувати термоелектричними властивостями полікристалів Bi₂Te₃ у температурному інтервалі 77-300 К, змінюючи ступінь відхилення від стехіометрії.

Ключові слова: Bi₂Te₃, Стехіометрія, Коефіцієнт Зеебека, Коефіцієнт Холла, Рухливість носіїв заряду, Температурні залежності.