

## Percolation effects and self-organization processes in $\text{Bi}_2(\text{Te}_{1-x}\text{Se}_x)_3$ solid solutions

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The room-temperature dependences of microhardness  $H$ , electrical conductivity  $\sigma$ , the Seebeck coefficient  $S$ , and thermoelectric power factor  $P$  on composition of  $\text{Bi}_2(\text{Te}_{1-x}\text{Se}_x)_3$  solid solutions were measured in the concentration range  $x = 0 - 0.07$ . In the intervals  $x = 0.0075 - 0.0175$  and  $x = 0.025 - 0.035$ , an anomalous decrease in  $H$  and  $S$  and increase in  $\sigma$  with increasing  $x$  were observed. The first concentration-dependent anomaly was attributed to critical phenomena, accompanying a percolation-type phase transition. The percolation threshold  $x_c$  and the radius of deformation spheres  $R_0$  around Se impurity atoms were estimated. The second anomaly is assumed to be connected with a short-range ordering in the solid solution. The non-monotonic character of the dependences of  $H$  on the load on an indenter, whose behavior depended on the impurity concentration, was attributed to the interaction of the deformation fields created by dislocations and impurity atoms.

**Keywords:** solid solutions, composition, microhardness, electrical conductivity, Seebeck coefficient, percolation, self-organization.

Получены зависимости микротвердости  $H$ , электропроводности  $\sigma$ , коэффициента Зеебека  $S$  и термоэлектрической мощности  $P$  от состава твердого раствора в концентрационном интервале  $x = 0 - 0.07$  при комнатной температуре. В интервалах  $x = 0.0075 - 0.0175$  и  $x = 0.025 - 0.035$  наблюдалось аномальное уменьшение  $H$  и  $S$  и увеличение  $\sigma$  с ростом  $x$ . Первая концентрационная аномалия связывалась с критическими явлениями, сопровождающими фазовый переход перколяционного типа. Проведена оценка порога перколяции  $x_c$  и радиуса деформационных сфер  $R_0$  вокруг примесных атомов Se. Предполагалось, что вторая аномалия связана с ближним упорядочением в твердом растворе. Немонотонный характер зависимостей  $H$  от величины нагрузки на индентор, зависящий от концентрации примесей, связывался с взаимодействием деформационных полей, создаваемых дислокациями и примесными атомами.

**Ефекти перколяції та процеси самоорганізації в  $\text{Bi}_2(\text{Te}_{1-x}\text{Se}_x)_3$  твердих розчинах.**  
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Одержано залежності микротвердості  $H$ , електропровідності  $\sigma$ , коефіцієнта Зеебека  $S$  і термоелектричної потужності  $P$  від складу твердого розчину у концентраційному інтервалі  $x = 0 - 0.07$  за кімнатної температури. В інтервалах  $x = 0.0075 - 0.0175$  та  $x = 0.025 - 0.035$  спостерігалось аномальне зменшення  $H$  і  $S$  та збільшення  $\sigma$  при зростанні  $x$ . Перша концентраційна аномалія пов'язувалась із критичними явищами, що супроводжують фазовий перехід перколяційного типу. Проведено оцінку порогу перколяції  $x_c$  та радіусу деформаційних сфер  $R_0$  навколо домішкових атомів Se. Припускалося, що друга аномалія пов'язана із ближнім впорядкуванням у твердому розчині. Немонотонний характер залежностей  $H$  від величини навантаження на індентор, який залежить від концентрації домішок, пов'язувався із взаємодією деформаційних полів, які створюються дислокаціями та домішковими атомами.

## 1. Introduction

The objects of the present study are  $\text{Bi}_2(\text{Te}_{1-x}\text{Se}_x)_3$  solid solutions, which are promising thermoelectric (TE) materials used in the manufacture of cooling devices [1, 2]. One of the basic methods of increasing the TE figure of merit  $Z$  of materials ( $Z = S^2\sigma/\lambda$ , where  $S$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity and  $\lambda$  is the thermal conductivity) that determines to a large extent the efficiency of a TE device, is "the solid solution method". This method, which was first proposed by A.F.Ioffe and has proved its fruitfulness, is based on the fact that the introduction of a second component into the matrix, leads to an increase in the ratio  $\sigma/\lambda$ , and accordingly  $Z$ , due to the difference in the de Broglie wavelengths of electrons and phonons. The possibility of practical use of TE materials is determined not only by the value of  $Z$ , but also by their mechanical properties, which include microhardness  $H$  — an important local characteristic of the material plastic properties [3, 4].

In a number of semiconductor solid solutions, in the region of low impurity contents, we detected concentration-dependent anomalies of various properties and attributed them to the manifestation of percolation effects [5, 6] that occur during the transition from dilute to concentrated solid solutions [7–9]. It is natural to assume that percolation effects, and their manifestation through anomalies in the concentration dependences of properties, occur when not only impurities but also other types of defects are introduced in solid solutions. For example, we observed similar effects when studying the dependences of properties on composition in the homogeneity regions of non-stoichiometric semiconductor phases in which cationic vacancies played the role of impurity atoms [10, 11]. Knowledge of the character of change in properties at low defect concentrations is extremely important not only for understanding general principles of physics and chemistry of solids but also for practical applications when materials properties are controlled by doping, formation of solid solutions or deviation from stoichiometry.

The goal of this work was to study the dependences of  $H$  and TE properties on the solid solution composition in the concentration range  $x = 0-0.07$  with a view to revealing the peculiarities of the manifestation of phase transitions. The  $\text{Bi}_2(\text{Te}_{1-x}\text{Se}_x)_3$  solid solutions are of substitutional type, in

which Se atoms substitute Te atoms in the anion sublattice of the crystal.

Microhardness and TE properties of  $\text{Bi}_2(\text{Te}_{1-x}\text{Se}_x)_3$  solid solutions as functions of composition were studied by a number of authors, but in their works, the incremental change in composition was rather large ( $\Delta x = 0.05 - 0.1$ ) [12–14]. Presently, to the best of our knowledge, there are no publications, in which the presence of concentration-dependent anomalies of properties in the range of small  $x$  was reported.

## 2. Experimental

The mixtures of high purity (99.999 % of the main element) Bi, Se, and Te with the corresponding component ratios were placed in quartz ampoules evacuated down to  $\sim 10^{-3}$  Pa, heated in a furnace to  $\sim 1200$  K and kept at this temperature for 5–6 h with simultaneous application of vibrational mixing. Then, the samples were annealed for 200 h at 820 K and cooled down to room temperature. The ten samples thus obtained were polycrystals of different compositions with an average grain size of  $\sim 200$   $\mu\text{m}$ . Microhardness  $H$  was measured on a PMT-3 device using the Vickers pyramid. The loading time was 10 s. Fresh chips of NaCl single crystals were used as a reference to calibrate the loading device. For measuring  $H$ , the surfaces of the specimens were carefully polished. It should be noted that  $\text{Bi}_2\text{Te}_3$  and crystals are anisotropic [1, 2]. That is why the values of  $H$  for grains with different lattice orientations were slightly different. It was shown that the size of the indentation and the values of  $H$  under the same load on indenter ( $P$ ) depend on the orientation of the grain (crystallite) relative to the surface. Therefore,  $H$  was measured over the entire surface of a sample on grains with different orientations, and the results were averaged. For each sample, at a given load on the indenter, at least 30 indentations were obtained. The relative mean-square fluctuation within a grain usually did not exceed  $\pm 3$  %, and over the entire surface —  $\sim 5$  %.

Before measuring the dependence of  $H$  on composition, the  $H(P)$  dependences in the interval of  $P = 0.0196 - 0.450$  N were obtained (Fig. 1). The  $H(P)$  dependences exhibited similar behavior for samples with different compositions:  $H$  increased with increasing  $P$ , which indicated the presence of a scale effect (the dependence of  $H$  on  $P$ ). At the same time, in most of the curves, there was a section in which  $H$  decreased

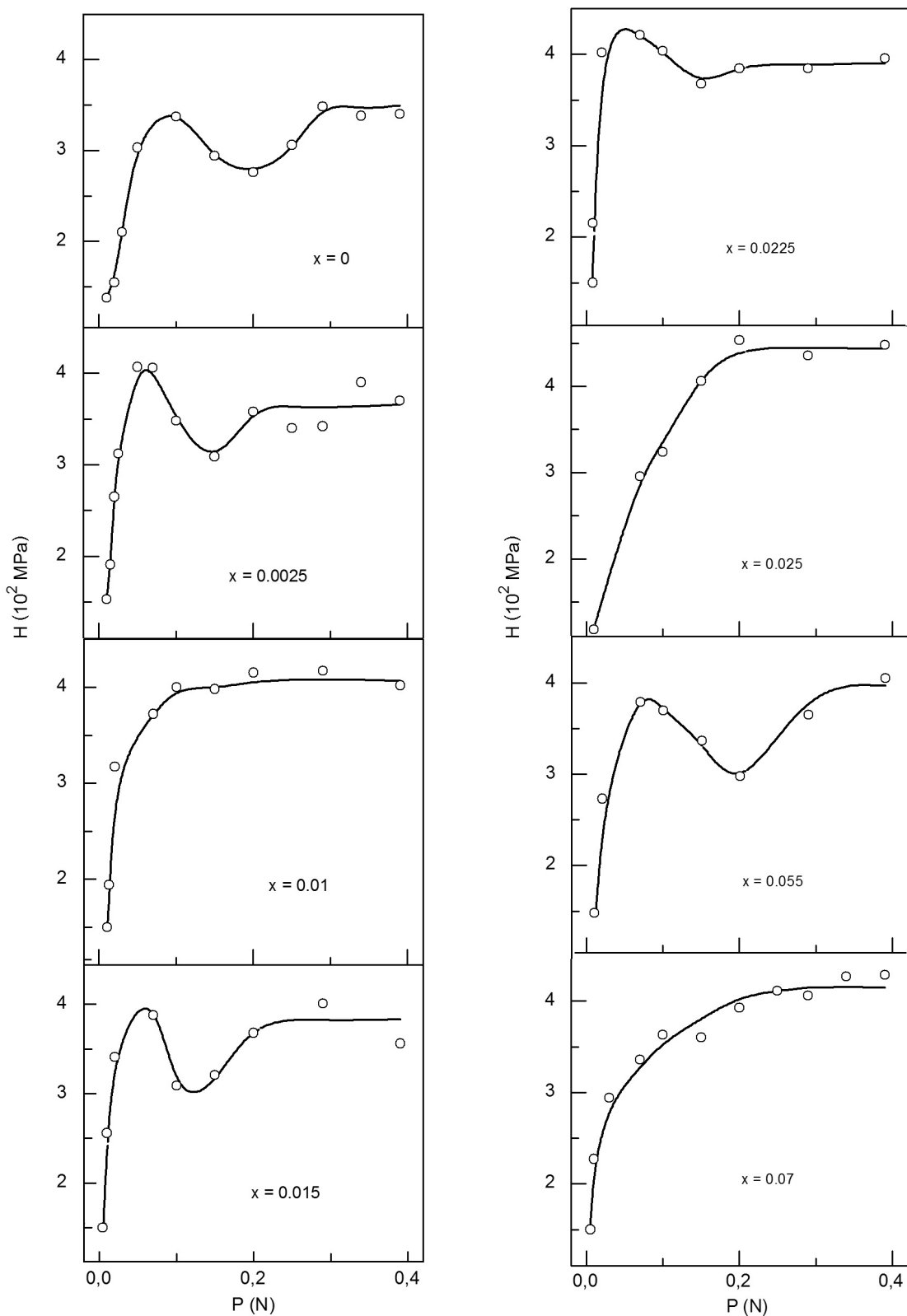


Fig. 1. The dependences of microhardness  $H$  on the load on an indenter  $P$  for  $\text{Bi}_2(\text{Te}_{1-x}\text{Se}_x)_3$  solid solutions with different concentrations  $x$ .

with  $P$  increasing although such section was practically absent for the samples with  $x = 0.01$ ,

$x = 0.03$  and  $x = 0.07$ . It can be seen that, starting from  $P \sim 0.25$  N (for some samples

from  $P \sim 0.35$  N),  $H$  practically does not depend on  $P$ . Thus, to exclude a scale effect when comparing the values of  $H$  for samples with different compositions,  $H$  should be measured under loads at which it does not depend on  $P$ . Therefore,  $H$  of all samples was measured under the load  $P = 0.39$  N. For some samples, measurements of  $H$  were carried out on the face (0001), because polycrystals are easily cleaved along the cleavage planes (0001). It turned out that the  $H$  values measured on ingots are greater than those measured on the freshly cleaved chips by approximately 10 %.

### 3. Results and discussion

In Fig. 2,a, the  $H(x)$  dependence for  $\text{Bi}_2(\text{Te}_{1-x}\text{Se}_x)_3$  solid solutions is presented. It can be seen that the dependence has a distinct non-monotonic character. When the first portions of Se (up to  $x \sim 0.01$ ) are introduced by  $\text{Te} \rightarrow \text{Se}$  substitution, the value of  $H$  increases, which indicates the crystal hardening. Solid solution hardening is a well known phenomenon and the main mechanism of this phenomenon is associated with the elastic interaction of the fields of dislocations and dissolved impurity atoms [15]. The latter block the movement of dislocations, and, as a result, the dislocation mobility decreases.

However, a further increase in  $x$ , in the interval  $x = 0.01 - 0.0175$ , leads to a decrease in  $H$ , which may be due to the self-organization of defects. Such self-organization can occur if the interaction between the impurity atoms spreads throughout the entire crystal, i.e. cooperative processes take place.

In the interval of  $x = 0.0175 - 0.02$   $H$  restores its growth, which can be attributed to the lattice disordering under further accumulation of defects. At still larger  $x$  (up to  $\sim 0.045$ ),  $H$  decreases, and then increases again.

Thus, instead of a monotonic increase in  $H$  with increasing impurity concentration, as it is assumed for ideal solid solutions, we observed an oscillatory dependence indicating a non-monotonic change in the defect structure.

In Figs. 2,b,c, the  $\sigma$  and  $S$  dependences on composition of the  $\text{Bi}_2(\text{Te}_{1-x}\text{Se}_x)_3$  solid solutions are presented. The measurements of the Seebeck coefficient showed that all investigated samples exhibited  $p$ -type conductivity, like the initial stoichiometric  $\text{Bi}_2\text{Te}_3$  polycrystal, which is consistent with the literature data [16]. Since the  $\text{Bi}_2\text{Se}_3$  compound is an isovalent and isomorphic impurity for  $\text{Bi}_2\text{Te}_3$  and these compounds form a continuous series of solid solutions, one could expect (like in the case of  $H$ ) the

$S(x)$  and  $\sigma(x)$  dependences to be monotonic curves. However, as is seen in Figs. 2,b,c these dependences exhibit a non-monotonic oscillating behavior similar to the  $H(x)$  dependence. The introduction of the first portions of  $\text{Bi}_2\text{Se}_3$  (up to  $x \sim 0.01$ ) leads to a decrease in  $\sigma$  (Fig. 2,b), which is typical of disordered solid solutions, when impurity atoms are centers of local distortions in the crystal lattice and sources of internal stress, and thus represent additional scattering centers for electrons, reducing their mobility and, as a result, electrical conductivity of the crystal.

The increase in  $S$  with increasing  $\text{Bi}_2\text{Se}_3$  concentration (Fig. 2,c) can be explained by a widening of the band gap  $E_g$  [17], which in turn leads to a decrease in the charge carrier concentration. It is known that for semiconductors with only one type of charge carriers, the Seebeck coefficient is defined by the following expression [18]:

$$S = \frac{k}{q} \left[ r + 2 + \ln \frac{2(2\pi m k T)^{3/2}}{nh^3} \right], \quad (1)$$

where  $q$ ,  $m$ , and  $n$  are the charge, effective mass, and concentration of charge carriers respectively,  $k$  is coefficient depending on the mechanism of scattering of charge carriers,  $T$  is the temperature. It follows from the equation 1 that a decrease in charge carrier concentration leads to an increase in  $S$ , which is actually observed.

Further increase in  $x$  results in a change in the character of the  $\sigma(x)$  and  $S(x)$  dependences. Both dependences exhibit an oscillatory behavior with pronounced extrema, the minima in the  $S(x)$  dependences approximately corresponding to the maxima in the  $\sigma(x)$  dependences and vice versa. Starting from  $x = 0.035 - 0.04$ ,  $\sigma$  decreases and  $S$  increases.

On the basis of the measured values of  $\sigma$  and  $S$ , the values of TE power factor  $P = S^2\sigma$  for the investigated samples were calculated (Fig. 2,d). Because of the non-monotonic character of the  $\sigma(x)$  and  $S(x)$  dependences, the  $P(x)$  dependence also exhibits an oscillatory behavior — sections in which  $P$  increases alternate with those in which  $P$  decreases. The maximum values of TE power factor ( $11.3 \cdot 10^{-4}$  and  $11.8 \cdot 10^{-4}$ )  $\text{W/m}\cdot\text{K}^2$  are attained at  $x \sim 0.015$  and  $x \sim 0.03$  respectively.

Analyzing the obtained  $H(P)$  dependences (Fig. 1), one can point to three main results: 1) for all compositions, scale effect occurs:  $H$  increases with increasing load; 2) for most of the compositions  $H$  first grows

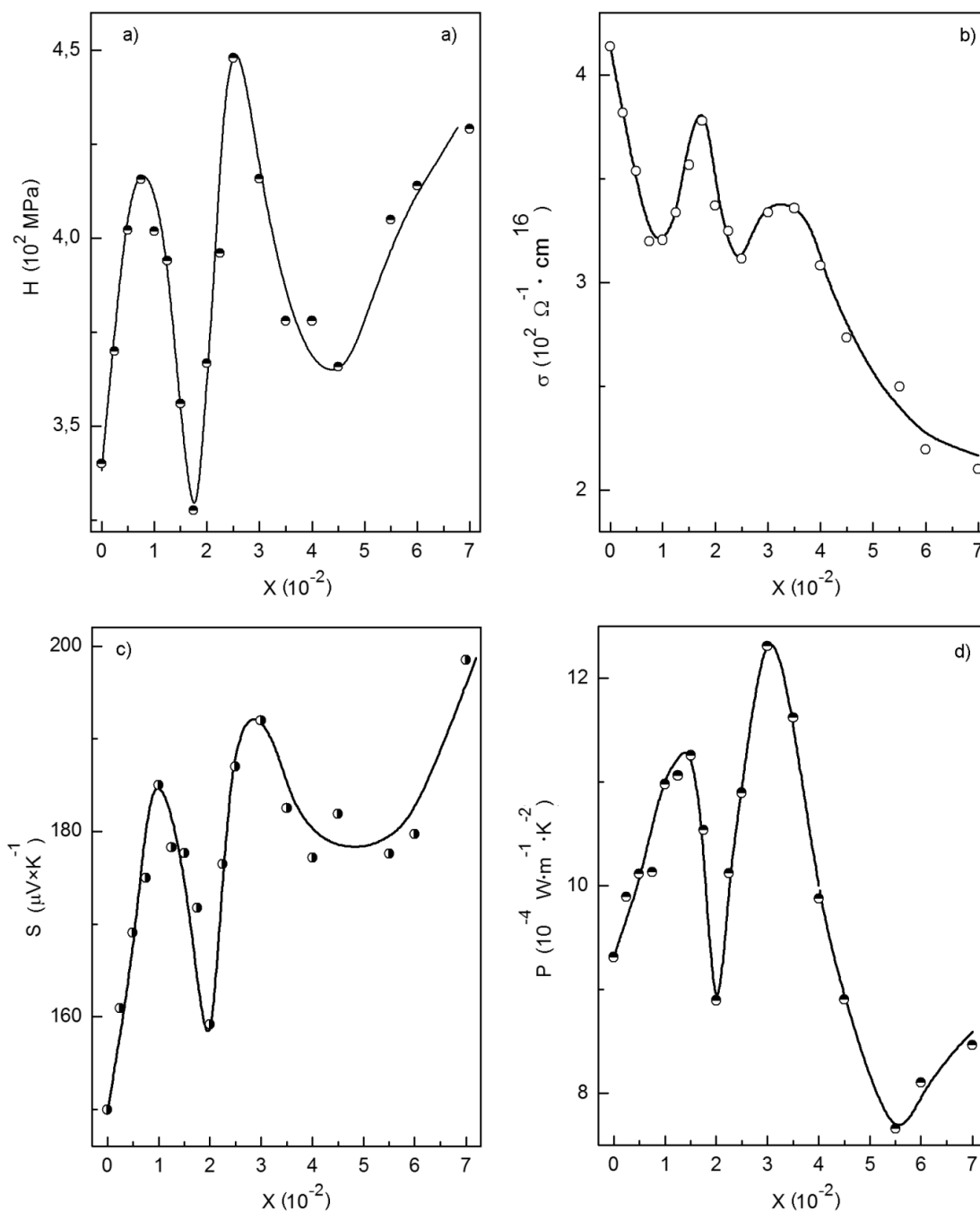


Fig. 2. The dependences of microhardness  $H$  (a), electrical conductivity  $\sigma$  (b), the Seebeck coefficient  $S$  (c) and thermoelectric power factor  $P$  (d) on the composition of the  $\text{Bi}_2(\text{Te}_{1-x}\text{Se}_x)_3$  solid solutions.

with increasing  $P$ , then decreases and eventually reaches saturation; 3) for some compositions in the  $H(P)$  dependences the decrease in  $H$  is not observed. Let us consider qualitatively the most likely factors determining the character of the  $H(P)$  dependences.

It is generally assumed that the scale effect occurs due to the difference in properties of the surface layer and the crystal interior. If this is the main reason, then in

the case when  $H$  in the surface layer is larger than  $H$  in the crystal interior, microhardness will decrease with increasing  $P$ . Conversely, if  $H$  in the surface layer is smaller than that in the crystal interior, an increase in  $P$  will lead to an increase in microhardness. At certain values of  $P$  the scale effect disappears and  $H$  does not depend on  $P$  any longer, the  $H(P)$  dependence representing a monotonic curve.

To explain the decrease in  $H$  with increasing  $P$ , which was observed for most of the compositions, one should take into account the following factor. At large concentrations of defects (impurities, structural defects of different types, for example, dislocations), the interaction between them can make a significant contribution to the crystal energy.

Today it is well known that plastic deformation in solids is the result of the movement and multiplication of dislocations, and the mechanical properties of the crystal are largely determined by the dislocation mobility [3, 4, 15]. The crystal plasticity is determined by the mechanisms of plastic deformation (dislocation, deformation twinning, etc.) and by the defect structure evolution under increasing load. Under small loads, it is dislocation plasticity that is the most likely mechanism, and all changes occurring in the dislocation system of the crystal under increasing load should be reflected in the  $H(P)$  dependence. When the dislocation density is large, they interact and at some critical density independent movement of separate dislocations becomes impossible. Dislocation systems start exhibiting collective properties, leading to the formation of ordered structures, such as dislocation ensembles [19]. In plastic materials, in which a high degree of deformation can be attained without destroying the crystal, the transition from micro- to macrohardness can be accompanied by phenomena caused by the collective processes in the deformation defect subsystem.

It follows from the data obtained that the  $H(P)$  dependences are not always monotonic functions, as it is usually assumed.

Taking into account these general considerations, we can explain the behavior of the  $H(P)$  dependences. First let us consider an impurity-free  $\text{Bi}_2\text{Te}_3$  crystal, in which there are only deformation fields formed by dislocations that appear under load. At a low loading (up to  $P \approx 0.05$  N) the number of dislocations is small, they do not interact with each other,  $H$  increases with increasing  $P$ , that is, strain hardening takes place. As  $P$  increases, the number of dislocations increases too, which results in their interaction and the formation of ordered dislocation structures. The emergence of such structures leads to a higher degree of ordering of the defect subsystem and, as a result, to the increased dislocation mobility. And this, in turn, determines the decrease in  $H$  (softening). Thus, it can be assumed that the decrease in  $H$  observed in the  $H(P)$  depend-

ences for most compositions is connected with the ordering of the dislocation structure resulting from the interaction among dislocations when their density becomes large. The minimum value of  $H$  corresponds to the highest degree of dislocation structure ordering. A further increase in load leads to the generation of structural defects of different types and  $H$  increases again.

One can expect that when Se impurity atoms are introduced in the anion sublattice, the character of the  $H(P)$  dependences will become more sophisticated, because apart from dislocations, impurity point defects appear in the crystal lattice and also create deformation fields, which interact with the deformation fields of dislocations. However, the behavior of the  $H(P)$  dependences does not change qualitatively compare to the impurity-free  $\text{Bi}_2\text{Te}_3$  crystal for all compositions except  $x = 0.01$ ,  $x = 0.025 - 0.03$  and  $x = 0.07$ . The  $H(P)$  dependences for these compositions do not contain a section in which  $H$  decreases under increasing load  $P$ :  $H$  increases with increasing  $P$ , until the curve reaches saturation. Let us also note that the concentrations  $x = 0.01$  and  $x = 0.025 - 0.03$  correspond to the compositions at which the extrema values of the properties are observed (Fig. 2) and ordering processes in the crystal lattice are possible (see below).

It is necessary to take into account that deformation fields of impurity atoms can interact not only with dislocation fields, but also among themselves, thus making possible self-organization processes in the impurity subsystem. Such processes can occur if the interaction among impurity atoms spreads over the entire crystal, i.e. cooperative processes take place.

In terms of percolation theory [5, 6], if we apply it to elastic interactions in the impurity subsystem of the crystal, such cooperative processes start when the percolation threshold  $x_c$  is reached and an uninterrupted chain of overlapping elastic fields of impurity atoms passing through the entire crystal (so-called "infinite cluster") is formed, facilitating the movement of dislocations. Taking into account that deformation fields diminish rapidly with the distance from the deformation source, one can consider elastic fields as short-range ones and introduce a radius of deformational interactions  $R_0$ . When impurity concentration is small ( $d > R_0$ , where  $d$  is the distance between impurity atoms), deformation spheres do not overlap and impurity atoms are randomly distributed over the host crys-

tal. As  $x$  increases, deformation spheres start to overlap, chains of interacting deformation spheres appear and, on reaching the critical impurity concentration  $x_c$ , the "infinite cluster" is formed. After percolation channels via deformational fields of separate atoms emerge, the compensation of microstresses leads to a sharp decrease in the overall level of elastic strains in the crystal lattice, which, in turn, results in a decrease in  $H$ , an increase in  $\sigma$ , and a drop in  $S$ . All this indicates that the impurity continuum has been formed. Within the framework of percolation theory, the formation of the "infinite cluster" at  $x_c$  is considered as a phase transition, which is accompanied by critical phenomena and qualitative changes in the properties of a solid solution. Further introduction of impurity atoms into this new medium causes new distortions in the crystal lattice and, consequently, a growth in  $H$  and  $S$ , and a simultaneous decrease in  $\sigma$ .

It is natural to assume that the percolation threshold  $x_c$  for deformation interactions in the  $\text{Bi}_2(\text{Te}_{1-x}\text{Se}_x)_3$  solid solution corresponds to the composition ( $x = 0.01$ ) at which the first minimum in the  $\sigma(x)$  dependence and the first maxima in the  $H(x)$  and  $S(x)$  dependences are observed. Knowing the value of the critical concentration  $x_c$ , one can calculate the radius of the impurity atom "action sphere"  $R_0$  from the condition:

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

where  $N_c$  is the average number of sphere centers per unit volume at the composition corresponding to the percolation threshold  $x_c$ . Using equation (2) we obtain that  $R_0 = 1.58 \text{ nm} = 3.61a$ , where  $a$  is the unit cell parameter  $a$  of a  $\text{Bi}_2\text{Te}_3$  hexagonal lattice. The effective value of  $x_c$  depends on the range of interactions in the system. A simple estimation taking into account parameters of the  $\text{Bi}_2\text{Te}_3$  crystal lattice and distances between atoms shows that the obtained value of  $R_0$  corresponds to approximately the seventh neighbor shell.

Thus, one can assume that the observed anomalous behavior of the concentration dependences of  $H$ ,  $S$  and  $\sigma$  near  $x = 0.01$  can be attributed to critical phenomena taking place under the transition from dilute to concentrated solid solutions.

After the formation of the impurity continuum at the critical concentration  $x_c$ , further increase in  $x$  leads to new distortions

in the crystal lattice, which, in turn, cause further decrease in  $\sigma$  and increase in  $H$  and  $S$  (Fig. 2,a,b,c). However, at still higher concentrations  $x$ , the behavior of the concentration dependences of  $H$ ,  $S$  and  $\sigma$  becomes anomalous again:  $H$  and  $S$  decrease and  $\sigma$  increases in the interval  $x = 0.025 - 0.045$ . One can suggest that this anomaly can be connected with a short-range ordering in the solid solution, for example, with the formation of  $\text{Bi}_2\text{Se}_3$  complexes. Thus, obviously, the processes of accumulation of defects (when  $H$  increases) and alternating with them processes of defect self-organization (when  $H$  decreases), play a major role in determining a non-monotonic character of the dependence of  $H$  on solid solution composition. Let us note that we observed a non-monotonic behavior of the concentration dependences of  $H$  and other properties in a number works [20–22].

The behavior of the  $H(P)$  dependences observed for the samples with  $x = 0.01, 0.03$  and  $0.07$ , can be attributed to the self-organization processes taking place in solid solutions at the indicated compositions. The mechanisms of the influence of these processes on the  $H(P)$  dependences require a special study.

One can draw a certain analogy between the  $H(P)$  and  $H(x)$  dependences. In the first case, the crystal is subjected to the influence of an external load  $P$ , whose increase leads to an increase in the dislocation density. Initially, when dislocations practically do not interact,  $H$  grows with increasing  $P$ . However, at a certain value of  $P$  the number of dislocations becomes so large that they start to interact with each other and order, their mobility increases, thus leading to a decrease in  $H$  (crystal softening). It can be assumed that there is a percolation threshold for dislocations too, when the interaction among dislocations spreads over the entire crystal. In the second case (the  $H(x)$  dependences), increasing impurity concentration also produces strains in the crystal lattice, but they are caused not by an external force but rather by the increasing number of impurity atoms creating deformation fields. On reaching the percolation threshold, when the interaction among impurities becomes cooperative, strains are released and crystal softening occurs. The phenomena caused by increasing load on the indenter and increasing impurity concentration differ only by the type of the defects formed: dislocations in the former case and impurity atoms in the latter.

#### 4. Conclusions

The analysis of the obtained dependences of microhardness  $H$ , electrical conductivity  $\sigma$ , Seebeck coefficient  $S$  and thermoelectric power factor  $P$  on composition of the polycrystalline solid solutions in the range of  $x = 0 - 0.07$  as well as the dependences of  $H$  on the load on indenter for solid solutions of different compositions allows us to formulate the following conclusions:

The  $H(x)$ ,  $\sigma(x)$ ,  $S(x)$ , and  $P(x)$  dependences have a non-monotonic oscillating character. Although, with increasing  $x$ ,  $H$  and  $S$  exhibit a generally increasing trend and  $\sigma$  a decreasing one, in the vicinity of  $x \sim 0.01$  and  $x \sim 0.025 - 0.03$ , there are maxima in the  $H(x)$  and  $S(x)$  dependences and minima in the  $\sigma(x)$  dependence.

The presence of extrema in the  $H(x)$ ,  $\sigma(x)$ ,  $S(x)$  dependences at  $x \sim 0.01$  is attributed to critical phenomena accompanying the percolation-type phase transition from dilute to concentrated solid solutions. An estimate of the radius  $R_0$  of the deformation sphere created by a Se impurity atom within the framework of percolation theory ( $R_0 = 1.58$  nm) shows that this value corresponds to approximately the seventh coordination sphere. The observed effect represents another confirmation of the suggestion about the universal character of critical phenomena that occur in solid solutions under the transition to an impurity continuum.

We assume that the existence of the extrema near  $x \sim 0.025 - 0.03$  is indicative of self-organization processes occurring in solid solutions, for example, a short-range ordering.

Although with increasing indentation load  $P$ ,  $H$  increased (the scale effect), for most of the compositions we observed a non-monotonicity in the  $H(P)$  dependences: first  $H$  increased, then dropped, after that increased again and eventually reached saturation (the absence of the scale effect). The decrease in  $H$  is attributed to the interaction among dislocations that occurs when their number grows with increasing load, and, possibly, the formation of dislocation ensembles. It is shown that there is an analogy between the  $H(x)$  and  $H(P)$  dependences.

The non-monotonic behavior of the concentration dependences of mechanical and thermoelectric properties observed in this work should be taken into consideration when modifying properties of materials by doping and forming solid solutions in a wide range of concentrations. The observed

regularities are apparently typical for other solid solutions as well.

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