

**THERMOELECTRIC AND MECHANICAL PROPERTIES
OF BISMUTH-DOPED LEAD TELLURIDE**

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- *The effect of elementary introduced Bi upon thermoelectric properties and microhardness of PbTe is investigated. Non-monotonous behaviour of PbTe properties dependence on bismuth content is established. Intricate behaviour of the dependences is associated with the modification of Bi dissolution pattern observed under composition variations as well as percolation effects and self-arrangement processes in the impurity subsystem of the crystal. Concentrations of Bi corresponding to maximum values of thermoelectric power are determined.*

Introduction

Semiconductor compound *PbTe*-based materials are widely used in thermoelectric devices, infrared sensors and IR sources; they are applied in holography etc. [1-3]. One of the principal methods of regulating the properties of these materials is doping and formation of solid solutions with wide concentration range. Bismuth is one of the most important *PbTe* dopants, bismuth doping allows obtaining such electron concentrations that can ensure maximum values of thermoelectric figure-of-merit in crystals and thin films, optimum parameters of *p-n* junctions in laser diodes etc.

PbTe doping with *Bi* can be performed in different ways. One can introduce elementary *Bi*, congruently melting Bi_2Te_3 compound, *BiTe* additive and the like into the solution. Development of the fundamental principles of oriented *PbTe* doping with bismuth is associated with the investigation of the effect of *Bi* introduced into *PbTe* under steady control upon various properties.

Several papers are devoted to the investigation of *PbTe*-based solid solutions in the ternary system of *Pb-Bi-Te* type. According to [4], *Pb-Bi-Te* system has two quasibinary sections, i. e. *PbTe-Bi₂Te₃* and *PbTe-Bi*, their state diagrams are presented in research papers [5] and [4], respectively. Besides, [4] also contains a state diagram of non-quasibinary *PbTe-BiTe* system. It was established that solubility of *Bi* [4] and *BiTe* [4, 6] in *PbTe* system does not exceed 1 at.%, while solubility of Bi_2Te_3 in *PbTe* system amounts to ~ 5 at.% [6, 7]. As it was demonstrated in [8], in *PbTe-BiTe* system with concentration in the range of 0-3 at.% *BiTe*, mechanical, galvanomagnetic and other properties do not follow monotonic pattern which is probably due to the percolation-type effects and complexation processes. Investigation of *PbTe* homogeneity region (HR) in *Pb-Bi-Te* ternary system [7] showed that introduction of *Bi* up to ~ 3 at.% broadens HR shifting it towards the increase of *Te* content; maximum extension of homogeneity region corresponds to *PbTe-Bi₂Te₃* section cut.

Presently, profound donor effect of *Bi* in *PbTe* system is universally recognized. According to [9-11], introduction of *Bi* into stoichiometric *p-PbTe* results in the change of polarity when *Bi* content is below 0.1 at.%. As it was displayed in [6], doping effect of *Bi* is more prominent along *PbTe-BiTe* section cut rather than along *PbTe-Bi₂Te₃* cut. In [12] these results are interpreted using two-region model of *PbTe* conductivity assuming reduction of energy disintegration of extremes at increasing *Bi* content. In [6, 8, 9, 12] it is established that under introduction of *BiTe* up to ~ 0.1 at.% *Bi*, each *Bi* atom supplies 1 electron, and under further increase of *Bi* content carrier concentration growth rate is reduced [6, 8, 12].

As far as we know, references contain no information regarding the pattern of the effect of elementary *Bi* upon *PbTe* properties. Meanwhile, this case has practical significance. One of the prevailing methods of doped single crystal growth is surface saturation with dopants and subsequent anneal-

ing at predetermined temperatures. The problem of interaction between *PbTe* and *Bi* also emerges when *PbTe<Bi>* films are obtained and doping is performed by supplementary sputtering of elementary *Bi* from the independent source. Certain authors have investigated *PbTe/Bi* superlattices and highlighted the prospects of their utilization for thermoelectric applications in the future. [13]. Development of heterojunction structure preparation method requires information concerning the character of interaction between *PbTe* and *Bi* on the junction and accompanying change of properties.

The aim of the present paper is to determine the pattern describing dependences of thermoelectric and mechanical properties of *PbTe* upon *Bi* content under varying alloy composition along *PbTe-Bi* cut in *Pb-Bi-Te* concentration triangle.

Experimental technique

(PbTe)_{100-x}Bi_x alloys ($x = 0\div 4$) were synthesized by alloying high-pure *Pb*, *Bi* and *Te* (not lower than 99.999 at.% of the main component) in the evacuated up to $\sim 10^{-1}$ Pa quartz vessels using vibration mixing. The samples were annealed at 820 K during 200 hours and cooled at switched off furnace rate. Monitoring of the sample homogeneity level by microhardness and microthermoemf proved that spread in the values of indicated parameters over the sample did not exceed their measuring error. Precipitations in the second phase (eutectic) were first detected at $x = 2$, which agrees well with the results [4].

Microhardness H was measured at room temperature with PMT-3 device using diamond cutting point at 0.49 H load. Loading period, load detention time and load removal time were each 10 s. The device was adjusted using fresh *NaCl* crystal chips. Surface preparation for H measurements (surfacing, abrasive polishing and etching with 15% *HNO₃* solution) was identical for all samples. Values of H were obtained by averaging of 30 imprints. Statistical processing of the results indicated that the value of relative mean-square fluctuation in the series of 30 measurements of H did not exceed ~ 1.0 %. In order to determine possible effect of non-identical conditions of microsection preparation in the process of H measurements upon H values we used three different samples made of one ingot. It was established that spread in H values over three different samples did not exceed the spread of values over each sample. Electrical conductivity σ and Hall coefficient R_H were measured using magnetostatic field method (~ 1 Tesla) and direct current in the sample to within $\sim 5\%$. Indium was used as contact material. Charge carrier concentration was calculated using the formula $n = r/(e \cdot R_H)$ assuming that Hall factor $r = 1$, while Hall mobility was determined by formula $\mu = R_H \cdot \sigma$. Seebeck coefficient was measured with regard to copper accurate within ~ 2 %.

Experimental results

Fig.1 represents dependence of microhardness upon *Bi* content. As we may see, introduction of the first doses of *Bi* brings forward sharp increase of H : when $x = 0.1$ microhardness grows by $\sim 30\%$ compared to the original composition (*PbTe*). However, when $x = 0.25$, H drops significantly, while when $x \sim 1.25\div 1.5$, H tends to increase under oscillating character of $H(x)$ dependence, and remains nearly constant since. Dotted line in Fig.1 represents monotone microhardness constituent in the oscillating region of $H(x)$ curve. The results of microstructural analysis and obtained dependence $H(x)$ enable us to conclude that solubility limit of *Bi* in *PbTe* after the applied thermal treatment does not exceed $x \sim 1.25\div 1.5$. On the other hand, complex and uncharacteristic for solid solutions behaviour of $H(x)$ dependence designates qualitative changes in the defect subsystem of the crystal under growth of *Bi* concentration.

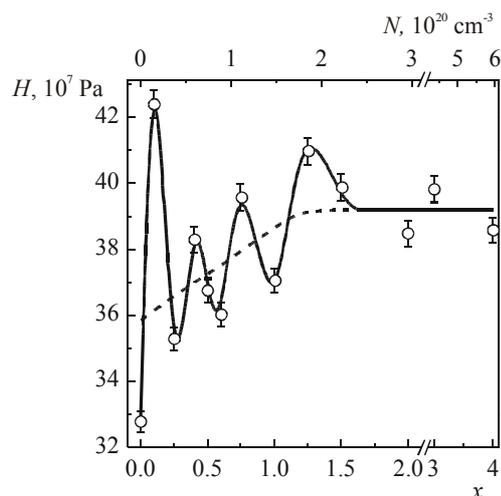


Fig.1. Dependence of microhardness H of $(PbTe)_{100-x}Bi_x$ crystal on bismuth content

Fig.2 (a) represents dependence of Hall coefficient on sample composition. Original stoichiometric $PbTe$ is p -conductive but when $x = 0.1$ we can observe polarity reversal. Estimation of the number of carriers supplied by each Bi atom in the region $x = 0-0.1$ yields ~ 3 carriers/atom. R_H grows within $x = 0.1 \div 0.25$ and drops again in the range $x = 0.25 \div 2.0$, though this time the rate is substantially lower than it was when first doses of Bi were introduced. In this region, each Bi atom supplies ~ 0.15 carrier. Beginning with $x \sim 2$, R_H remains practically constant.

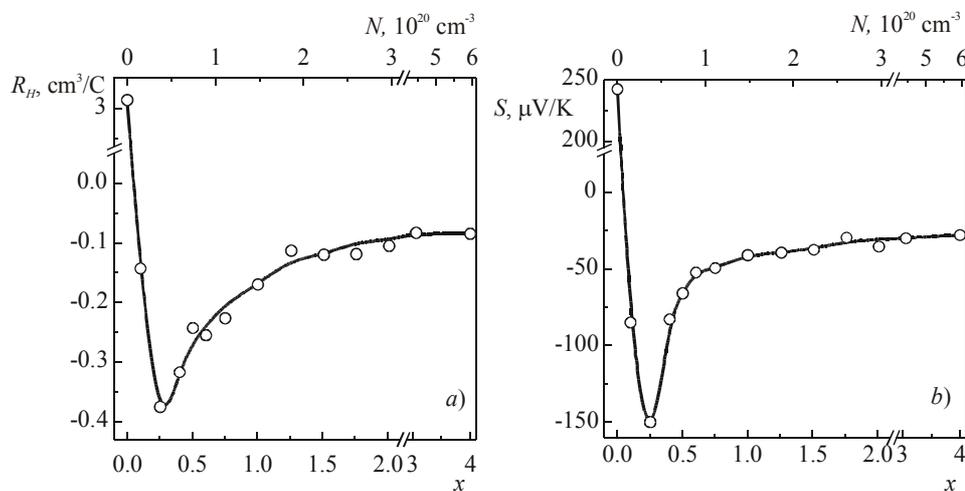


Fig.2 Dependences of Hall coefficient R_H (a) and thermoEMF coefficient S (b) of $(PbTe)_{100-x}Bi_x$ crystals on bismuth content

Dependence $S(x)$ is characterized by similar behaviour (see Fig. 2 (b)). When $x = 0.1$, Seebeck coefficient is negative and reaches maximum when $x = 0.25$. Then S drops to $\sim 50 \mu V/K$ when $x \sim 0.6$, and gradually decreases since.

Fig.3 represents dependences of carrier mobility (Fig.3, a) and concentration (Fig.3, b) on Bi content. Like curve $H(x)$, the dependence $\mu(x)$ does not follow monotone pattern which is indicative of complex defect formation processes occurring in $PbTe$ crystal lattice after Bi is introduced. When $x = 0.1$, carrier mobility decreases compared to μ of stoichiometric p - $PbTe$ (which is evidently associated with impurity scattering and substantial heterogeneity of the electrical image in the region of polarity

reversal) but when $x = 0.25$ μ increases dramatically. It can be attributed either to reduced concentration of charge carriers and corresponding decrease of degeneration observed within $x = 0.1 \div 0.25$ or different defect formation procedure which is confirmed by H drop in the given x range. Abnormal (in sight of ordinary solid solutions) growth of μ under increasing Bi concentration accompanied by dramatic decrease of microhardness (see Fig. 1) occurs within $x = 0.4 \div 0.75$. Taking into consideration the absence of peculiar behaviour of $R_H(x)$ dependence in this case, and abnormal behaviour of $H(x)$ dependence we may conclude that growth of μ within $x = 0.4 \div 0.75$ is associated not with the change of degeneration factor, but with a change of carrier scattering pattern resulting from the changes in defect subsystem.

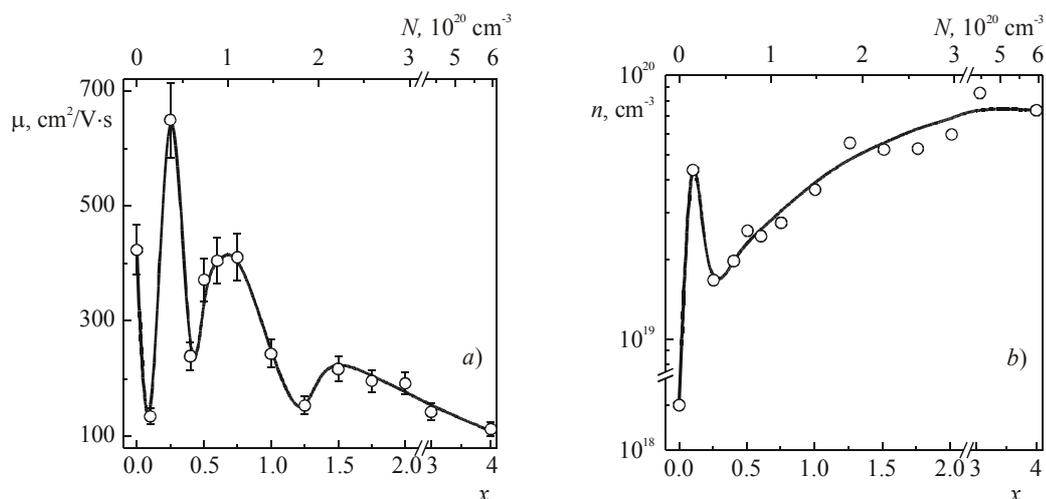


Fig.3. Dependence of mobility (a) and concentration (b) of charge carriers in $(PbTe)_{100-x}Bi_x$ crystals on bismuth content

Fig. 4 shows dependence of thermoelectric power P on Bi content. It is evident that P reaches maximum ($P = 39 \cdot 10^{-4} \text{ W/m K}^2$) when $x \approx 0.25$.

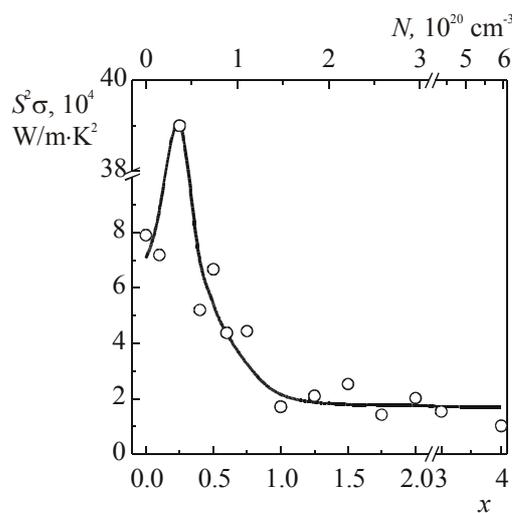


Fig.4. Dependence of thermoelectric power $P = S^2\sigma$ of $(PbTe)_{100-x}Bi_x$ crystals on bismuth content

Discussion of the results

Thus, both dependences of microhardness and galvanomagnetic and thermoelectric properties of *PbTe* on the content of elementary *Bi* are indicative of complex defect formation processes occurring in *PbTe* crystal lattice after *Bi* is introduced.

Among principal mechanisms regulating dissolution of cation-forming impurities in stoichiometric compounds are insertion of impurity atoms into interstitial sites or filling cationic sublattice sites with impurity atoms and formation of vacant sites in anionic sublattice. The above mechanisms can be supplemented by the mechanisms related to the formation of anti-structural defects (*Bi_{Te}*). In semiconductor crystals with traditionally small coordination numbers and corresponding sufficiently loose structure enthalpy of atomic interstitial site formation is comparable to vacant site formation. As a result, internodal atoms in semiconductors play more important role than they do in metals which are characterized by densely packed atomic structures. When impurities are introduced into non-stoichiometric compound, additional dissolution mechanisms develop due to interaction between intrinsic and impurity defects. As we have established earlier [14-17], principal mechanism regulating dissolution of elementary impurities in *SnTe* and *GeTe* compounds with highly-concentrated (~1 at.%) non-stoichiometric vacant lattice sites is filling of cationic vacant sites with impurity atoms entailing decrease of microhardness, carrier concentration depletion and growth of their mobility accompanied by the increase of lattice conductivity. For certain impurities along with dissolution in the vacant sites we observed insertion of the first doses of impurity atoms into interstitial sites. In some cases the above effect disappeared after the sample was annealed.

PbTe has much narrower (compared to *SnTe* and *GeTe*) homogeneity region; its extension in *Pb-Te* system does not exceed several hundredth at.% *Te* [18]. Principal defects of non-stoichiometric *PbTe* are *Pb* and *Te* vacant sites and internodal *Pb* atoms (from the side of excessive *Pb*). Traditionally, stoichiometric composition of *PbTe* is characterized by hole conductivity which is due to displacement of peaks on solidus and liquidus curves and their shift towards excessive *Te*. Concentration of cationic vacant sites in non-stoichiometric *PbTe* does not exceed ~ 0.02 at.% [18].

Dramatic increase of *H* under small *Bi* impurities ($x = 0 \div 0.1$) is indicative of substantial lattice deformation while decrease of μ indicates improved charge carrier scattering over impurity ions. In this connection we may assume that first doses of *Bi* atoms are most likely to enter the lattice following insertion pattern with localization in the interstitial lattice sites. This assumption can be substantiated by the fact that in the given *x* range each *Bi* atom supplies ~ 3 free electrons, i. e. it is the most electrically active donor dopant compared to other methods of introducing *Bi* atoms into *PbTe* crystal, for instance, in the form of *BiTe* or *Bi₂Te₃* [6-11]. Besides, it should be noted that processes of impurity atoms dislocation with regard to principal structural sites when their quantity is small and interaction between impurity atoms is negligible are stimulated by sharp growth of configuration entropy which is not balanced by the growth of crystal intrinsic energy observed when first impurity doses are introduced. Since bonding energy of impurity atom is lower than bonding energy of ground atom (at least, in the low concentration region of impurity), impurity atoms will be dislocated in the first place.

Under certain impurity concentration further occupation of interstitial sites becomes thermodynamically disadvantageous. Two solutions are possible in this case: either dissolution pattern should be changed or *Bi* should be precipitated in the second phase. However, occupation of cationic vacant sites formed as the result of stoichiometric deviation with *Bi* atoms or completion of cationic sublattice with *Bi* atoms accompanied by concurrent formation of vacant sites in anionic sublattice is also conceivable.

Considering short-acting effect of deformation fields generated by impurity atoms and high level of charge shielding in the compounds of IV-VI type (in view of high values of static electric

permittivity) [3, 18, 19] we can investigate this problem in the context of short-range theory, for instance, percolation theory [20]. Under growing concentration of *Bi* atoms, force fields (deformation field, Coulomb field etc.) generated by individual impurity atoms begin to overlap and under certain critical concentration x_c (percolation limit [20]) percolation passages are formed. As we have demonstrated earlier, these processes are traditionally accompanied by decrease of the total level of elastic stresses in the lattice and drop of microhardness [21-23]. Formation of percolation passages stimulates cooperative self-arrangement processes in the impurity defect subsystem which can be reduced to both redistribution of impurity atoms over the lattice interstitial sites (far or near ordering) and qualitative change of impurity atom localization behaviour.

Taking into consideration the above information, we may assume that up to $x = 0.1$ *Bi* atoms are mainly inserted into interstitial sites as they do not interact between each other or with available cationic vacant sites. With increasing *Bi* content, percolation passages are formed, and therefore favorable environment for self-arrangement processes is established. Due to this fact, H and n are decreasing critically while μ grows up to $x \sim 0.25$ (see Figs. 1, 3). Reduction of electron concentration at increasing x up to $x = 0.25$ can be attributed to partial liberation of impurity atoms in internodal sites and their localization in cationic vacant sites formed in stoichiometric *PbTe* as the result of stoichiometric deviation and/or occupation of cationic sites with concurrent formation of vacant sites in tellurium sublattice. In this case electrical activity of *Bi* atoms will be lower than electrical activity observed when *Bi* atoms enter interstitial sites.

After the processes of lattice rearrangement are completed at $x \sim 0.25$, subsequent introduction of *Bi* occurs in the context of new “self-arranged” structure while the pattern of *Bi* atoms insertion into the lattice is changed and *Bi* exhibits low electrical activity (each *Bi* atom supplies only ~ 0.15 carrier). Probably, a portion of *Bi* atoms is introduced into interstitial sites in unionized state. Such processes can precede preliminary liberation stage when clusters of non-liberated phase (bismuth) still retaining lattice bonding are formed. Moreover, we shouldn't exclude growing probability of amphoteric effect of *Bi* when *Bi* atoms concurrently occupy both cationic and anionic sites in Bi^{3+} and Bi^{3-} states, respectively, while general electrical neutrality of the lattice is maintained. The authors relied upon this pattern [24] for explanation of abnormal dependence of electron concentration in *PbTe-BiTe* alloys upon excessive *Te* content.

Oscillating behaviour of $H(x)$ and $\mu(x)$ dependences within $x=0.25\div 1.5$ is apparently due to new self-arrangement processes occurring in the defect subsystem of the crystal under certain *Bi* concentrations and alternating with processes of new defects accumulation against the background of well-ordered medium. At self-arrangement stage H drops while μ grows. Intermediate well-ordered structural states are possible even at the preliminary liberation stage and oversaturated solid solution decomposition stage. Determination of specific defect formation patterns within $x = 0.25\div 1.5$ requires special structural investigations.

Comparison of maximum values of thermoelectric power obtained in the present investigation and our research [8] dedicated to the investigation of thermoelectric properties of *PbTe-BiTe* alloys demonstrates close proximity of these values. Therefore, the choice of the most suitable method used for *PbTe* doping with bismuth in order to obtain optimum electron concentration values will be stipulated by complementary factors, e. g. thermal conductivity, degree of reproducibility and stability of parameters, degree of homogeneity of the samples, etc. For instance, in [25] it was highlighted that introduction of *Bi* as a dopant for Bi_2Te_3 system results in both weaker (compared to *BiTe* dopant) doping effect and considerable spacious heterogeneity of *PbTe* samples.

The findings and results of the investigation can be used as a basis for controlled doping of *PbTe* crystals and films by introduction of elementary bismuth. Furthermore, they can be applied to

predict changes of properties observed under interaction between *PbTe* and *Bi* in heterojunction structures.

Conclusions

The paper pioneers investigation of the effect of *Bi* element introduced into $(PbTe)_{100-x}Bi_x$ system upon thermoelectric and mechanical properties of *PbTe*.

Non-monotonous behaviour of *PbTe* properties dependence on bismuth content was determined. It is associated with the change of *Bi* dissolution pattern under varying composition, percolation effects and self-arrangement processes in the impurity subsystem of the crystal.

Maximum values of thermoelectric power ($P = 39 \cdot 10^{-4} \text{ W/m}\cdot\text{K}^2$) observed at $x \sim 0.25$ actually coincide with peak *P* values obtained under introduction of *BiTe* dopant in *PbTe*.

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