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THERMOELECTRIC PROPERTIES OF POLYCRYSTALLINE $Bi_{1-x}Sb_x$ SOLID SOLUTIONS IN THE CONCENTRATION RANGE $x = 0 – 0.25$

A detailed investigation of the dependence of thermoelectric properties of polycrystalline $Bi_{1-x}Sb_x$ solid solutions on composition in a wide concentration range ($x = 0 – 0.25$) was performed at room temperature. The objects of study were cast samples of various composition obtained by ampoule method in one technological cycle consisting in cooling of ampoules with melts in the air and subsequent long homogenizing annealing at temperature (520 ± 5) K for 720 hours. It was shown that the composition dependences of properties are of clearly expressed non-monotonic type. The presence of concentration anomalies of thermoelectric properties was confirmed that had been earlier observed in the range $x = 0 – 0.1$ on cast samples after different kinds of thermal treatment and interpreted as manifestation of electron phase transitions. A complicated nature of dependences at $x > 0.1$ is attributable to qualitative changes in $Bi_{1-x}Sb_x$ band structure at certain critical compositions, a change in relative contribution to conductivity of charge carriers from different energy bands with a change in antimony concentration and high sensitivity of energy spectrum and physical properties of $Bi_{1-x}Sb_x$ κ to external effects.

Key words: bismuth-antimony solid solution, composition, thermoelectric properties, electronic transition, critical phenomena.

Introduction

Solid solutions formed by *Bi* and *Sb* semimetals are known as the best thermoelectric (TE) materials of *n*-type and promising thermomagnetic materials for temperatures below ~ 150 K [1 – 4]. Only in these materials the highest values of TE figure of merit $Z = (S^2 \sigma) / \lambda$ are achieved, where *S* is the Seebeck coefficient, σ is electric conductivity and λ is thermal conductivity ($Z = (6 \div 7) \cdot 10^{-3}$ K^{-1}). Recently there has been a surge of interest in studying the properties of $Bi_{1-x}Sb_x$ crystals and thin films due to observation in $Bi_{1-x}Sb_x$ of peculiar properties typic al of 3D-topological insulators [5, 6] and suggested proposals on the possibility of using these properties when creating high-performance TE materials [7].

Possessing close values of atomic radii, crystalline structures and electronic configurations of the same type, *Bi* and *Sb* semimetals form a continuous series of solid solutions whose band structure with a change of composition is varied in a complicated way [1 – 4, 8]. Fig. 1 schematically represents the accepted structure of energy bands of $Bi_{1-x}Sb_x$ solid solutions at 0 K. In pure *Bi* there is a band of "light" (L_a) and "heavy" (*T*) holes, and as a result of overlapping the hole *T* and electron L_s bands, bismuth demonstrates semimetal properties. Similar band structure is inherent in antimony where the band of "heavy" holes *H* and electron band L_a overlap. Adding of antimony to bismuth causes approach of bands L_s and L_a, at $x = 0.03 \div 0.04$ the energy gap between them E_g vanishes, the gapless state is realized, the bands L_s and L_a are inverted, and with a further increase of *x* the gap between them again increases. Simultaneously with increase in *Sb* concentration, the top of valence band *T* shifts down the energy with respect to the bottom of conduction band L_s, leading to reduced overlapping of *T* and L_s bands, and with concentration $x = 0.06 \div 0.07$ the overlapping of bands disappears and semimetal-indirect-gap semiconductor transition takes place whose energy gap is determined by the position of *T* and L_a bands. As long as with further increase of *x* the top of *T* bands continues shifting down the energy, at $x = 0.08 \div 0.09$ the tops of *T* and L_s valence bands coincide and in the concentration range $x \cong 0.09 – 0.15$ the energy gap is determined by the distance between bands L_s and L_a i.e. it becomes a direct-gap semiconductor. At $x = 0.15 \div 0.17$ the tops of bands L_s and *H* coincide, and with subsequent growth of *Sb* concentration (up to $x \sim 0.22$) the energy gap is determined by the distance between L_a and *H* bands, and it again becomes an indirect-gap semiconductor. Maximum value of the energy gap in semiconductor region ($E_g \sim 0.025$ eV) is achieved near $x = 0.15 \div 0.17$, when the tops of L_s and *H*-bands coincide, following which the energy gap is reduced, i.e. $Bi_{1-x}Sb_x$ solid solutions in semiconductor region refer to narrow-gap semiconductors. At $x \sim 0.22$ the tops of *H* and L_a bands are set on the same level, semiconductor-semimetal transition is realized and at $x > 0.22$ $Bi_{1-x}Sb_x$ solid solutions acquire semimetallic properties. Their band structure is qualitatively similar to the band structure of pure antimony with localization of charge carriers at points *L* (electrons) and *H* (holes) of the Brillouin zone [1 – 4, 8]. High nonparabolicity of electron *L* – bands, strong temperature dependences of band parameters (finally not reliably established to date) largely complicate the interpretation of kinetic properties even at sufficiently low temperatures.

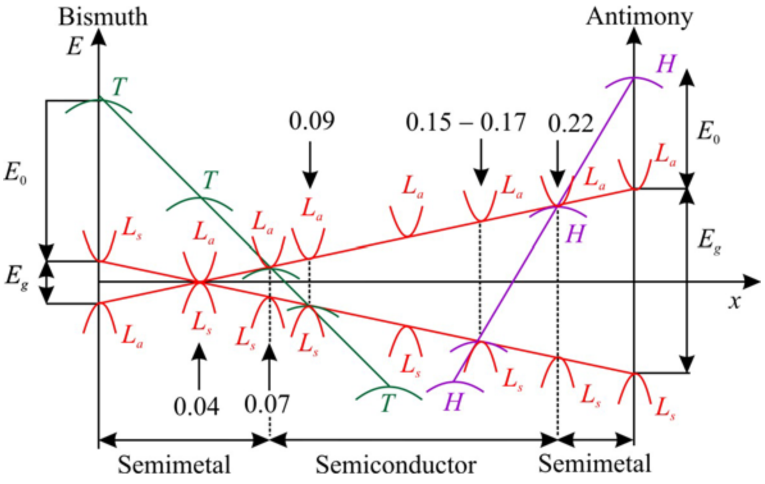

Fig. 1. Schematic of arrangement of energy bands in $Bi_{1-x}Sb_x$ solid solutions at 0 K [2].

The majority of studies on TE properties of $Bi_{1-x}Sb_x$ were performed on single-crystal samples [9 – 25] with a large concentration step. It was established that the dependences of electric conductivity $\sigma(x)$ and thermal conductivity $\lambda(x)$ are curves with a minimum in semiconductor region [9 – 20], and the dependences of the Hall coefficient $R_H(x)$ and the Seebeck coefficient $S(x)$ are curves with a maximum at the largest values of E_g [8, 9, 12 – 15, 17 – 20]. The authors of [24] on the dependence $\sigma(x)$ for $Bi_{1-x}Sb_x$ single crystals discovered an abnormal reduction of σ close to $x \sim 0.03$. According to different authors, the type of dependence of charge carriers on composition $\mu(x)$ is different. For instance, in conformity with [9, 22, 23], with increase in *Sb* concentration to $x = 0.3$, the value of μ is decreased for single crystals, and according to [26, 27] it is also observed for polycrystals. At the same time, for single crystals [13] and polycrystals [28, 29] mobility growth was discovered in the concentration ranges $x = 0 – 0.08$ [13], $x = 0 – 0.10$ [28] and $x = 0.08 – 0.10$ [29].

The authors of [21, 25] reported on having discovered for two $Bi_{1-x}Sb_x$ single crystals two maxima on the dependence $Z(x)$ at $T \sim 70$ K [21], ~ 82 K and ~ 95 K [25] close to compositions $x = 0.09$ and 0.16, whereby the peaks of T and H bands are on the same level with L bands. The authors of [21, 25] made an assumption that the observed dependence $Z(x)$ is caused by interband scattering of holes that takes place at transitions between the bands of "light" and "heavy" holes. Within the interval $x = 0.09 – 0.16$ the interband scattering is maximum, when the band extrema of "heavy" holes (T and H) coincide with the band extremum of "light" holes, which takes place close to compositions $x = 0.09$ and 0.16. It was noted that at higher temperatures maxima are not seen, and at room temperature a very weak dependence $Z(x)$ is observed.

The works dedicated to studying TE properties of $Bi_{1-x}Sb_x$ polycrystals mostly investigated pressed samples, and the object of study were either individual compositions [35 – 45] or alloys in the narrow range of compositions [31 – 34], or $Bi_{1-x}Sb_x$ solid solutions with a large step of Sb concentration [26 – 30]. It was established that the type of concentration and temperature dependences of TE properties of $Bi_{1-x}Sb_x$ polycrystals and single crystals is mainly similar [26 – 34], though the properties of polycrystals are essentially affected by grain size d: with a decrease in d the values of σ and λ are reduced, and the values of S are increased [37 – 45]. The latter fact was attributed [40] to reduction of relaxation time of charge carriers due to additional scattering at grain boundaries. In [37 – 39] it was shown that at $d > 200$ μm the values of σ and λ of $Bi_{1-x}Sb_x$ polycrystals approach the values of σ and λ for single crystals measured along the direction perpendicular to trigonal axis, and the values of the Seebeck coefficient are less than the values corresponding to S of single crystals. At grain size $d \sim 2.5$ μm [38, 39], ~ 10 μm [40] and ~ 0.05 μm [45] in $Bi_{1-x}Sb_x$ polycrystals in the range of compositions $x = 0.12 – 0.15$ the values of $Z = (0.9 – 1.1) \cdot 10^{-3}$ K^{-1} are achieved at 300 K. Maximum value of $Z = 1.5\ 10^{-3}$ K^{-1} at room temperature was obtained for $Bi_{85}Sb_{15}$ polycrystals with grain size $d \sim 0.04$ μm, made by pressing method at 523 K for 20 min under pressure 6 GPa [44, 45].

In [46 – 55] we studied $Bi_{1-x}Sb_x$ polycrystals with antimony content not exceeding $x = 0.12$, obtained by melting Bi and Sb in evacuated quartz ampoules with subsequent annealing at temperature 520 K. In addition to cast samples, we also prepared cold pressed samples under pressure 400 MPa, which after pressing were annealed for 250 hours [49 – 51]. It was shown [49] that the time of annealing of cast samples, as well as transition from cast to pressed samples practically does not affect the values of S and that annealing of both cast and pressed samples leads to electric conductivity and charge carrier increase, defining Z increase. On the dependences of unit cell parameters [47, 53], microhardness [48, 49, 54], thermal conductivity [52], heat capacity [55], TE and galvanomagnetic properties [46 – 51] on Sb concentration close to compositions $x = 0.01$, 0.03 and 0.06 we discovered anomalous areas which we attributed to critical phenomena accompanying percolation-type transition from diluted to concentrated solid solutions, transition to gapless state and semimetal-semiconductor transition, respectively. The dependences $Z(x)$ also were of non-monotonic type. It was established that a change in sample preparation technology does not affect the existence of concentration anomalies of TE and galvanomagnetic properties.

However, in [46 – 53] $Bi_{1-x}Sb_x$ polycrystals were studied in different concentration ranges: $x < 0.02$ [51], $x < 0.05$ [48], $x = 0.01 – 0.05$ [49], $x < 0.09$ [47, 50, 52, 53], $x < 0.12$ [46, 54], and cast samples were distinct in annealing times after synthesis: ~ 100 h [48], ~ 200 h [46 – 48, 50, 51], ~ 1200 h [49, 50, 51], 720 h [52 – 54]. Moreover, said publications studied various properties which further complicates comparing the results of different works. As regards the values of TE figure of merit, the values of Z were generally estimated in these works with the use of thermal conductivity values obtained for single crystals; only in [52] the values of λ were measured for polycrystalline pressed samples in the composition range $x = 0 – 0.09$ and it was shown that these values are close to those obtained by averaging λ values of single crystals measured along the trigonal axis and perpendicular to this direction.

In connection with the above it is interesting to study TE properties depending on the composition of $Bi_{1-x}Sb_x$ polycrystals prepared over a wide concentration range and under identical technological conditions.

It determined the main tasks set in the present paper: 1) to increase the number of various investigated compositions of $Bi_{1-x}Sb_x$ for greater probability of revealing the specific features on the concentration dependences of properties; 2) to get samples of various composition not just under strictly identical conditions (like, for instance, growing single crystals of various composition), but in one technological cycle; 3) to study a wide composition range ($x = 0 – 0.25$) covering semimetallic and semiconductor areas and allowing to trace the influence of qualitative change of electronic structure with a change in composition on the properties; 4) to use cast polycrystalline samples as the objects for study, unlike the majority of works which studied either single crystals or pressed samples.

From the results obtained in this paper it follows that with a detailed investigation of TE properties of polycrystalline $Bi_{1-x}Sb_x$ cast samples even at room temperature, apart from the concentration anomalies of TE properties in the range $x = 0 – 0.1$ that we had discovered earlier, one can reveal a non-monotonic type of TE properties variation with composition in the concentration range $x > 0.1$ related to peculiarities of variation in the band structure of $Bi_{1-x}Sb_x$ solid solutions with a change in composition (redistribution of charge carriers in different energy bands (L, T, H), interband scattering, etc).

Experimental procedure

Polycrystalline cast samples of $Bi_{1-x}Sb_x$ ($x = 0 – 0.25$) solid solutions were obtained from high-purity (not less than 99.999 % of the basic component) Bi and Sb elements by melting them in evacuated quartz ampoules at temperature (1020 ± 10) K, holding in the melt for 5 hours with the use of vibratory agitation. With a view to obtain samples with small grain size (to accelerate diffusion processes in solid state), the melt was subject to quenching in the air, following which the samples were again placed into furnace and annealed for 720 hours at temperature (520 ± 5) K for homogenization of alloys and to obtain compositionally uniform ingots. In one technological process there were simultaneously synthesized and thermally treated 30 samples of various composition with concentration step from $\Delta x = 0.0025$ to $\Delta x = 0.02$. In [52], we used a similar thermal treatment in the preparation of cast $Bi_{1-x}Sb_x$ alloys in the concentration range $x < 0.1$, however, synthesized samples were then subject to cold pressing under 400 MPa and subsequent annealing for 250 hours, and on these samples measurements of thermal conductivity and other TE properties were made.

In the present paper, measurements of TE and galvanomagnetic properties were made on the cast samples. For this purpose, samples in the shape of parallelepipeds of size 10 × 3 × 2 mm were cut from the resulting ingots to measure σ and R_H, and in the shape of cylinders of height 5 mm and diameter 15 mm to measure λ and S. The Seebeck coefficient S was measured by compensation method with respect to copper electrodes with an accuracy of ± 3 %, and R_H and σ were measured by standard *dc* method in a magnetic field $B = 0.05$ T, which for $Bi_{1-x}Sb_x$ solid solutions at 300 K is a weak magnetic field [55], with an accuracy not more than 5 %. Thermal conductivity λ was measured by dynamic calorimeter method on the IT – λ - 400 installation in the temperature range 170 – 520 K [56]. The technique for measurement of λ is described in detail in [52]. For each sample the temperature dependences λ(T) were obtained at least twice, and the difference between the resulting values of λ did not exceed 5 %, which corresponded to thermal conductivity measurement error. By the results of measuring λ a dependence λ(x) was constructed at $T = 300$ K. The resulting values of σ, S and λ were used to calculate the values of TE figure of merit Z.

Experimental results

Fig. 2*a* – fig. 2*c* represent the dependences $S(x)$, $R_H(x)$ and $\sigma(x)$ obtained for $Bi_{1-x}Sb_x$ alloys and having, as we can see, a non-monotonic nature, uncommon for continuous solid solution.

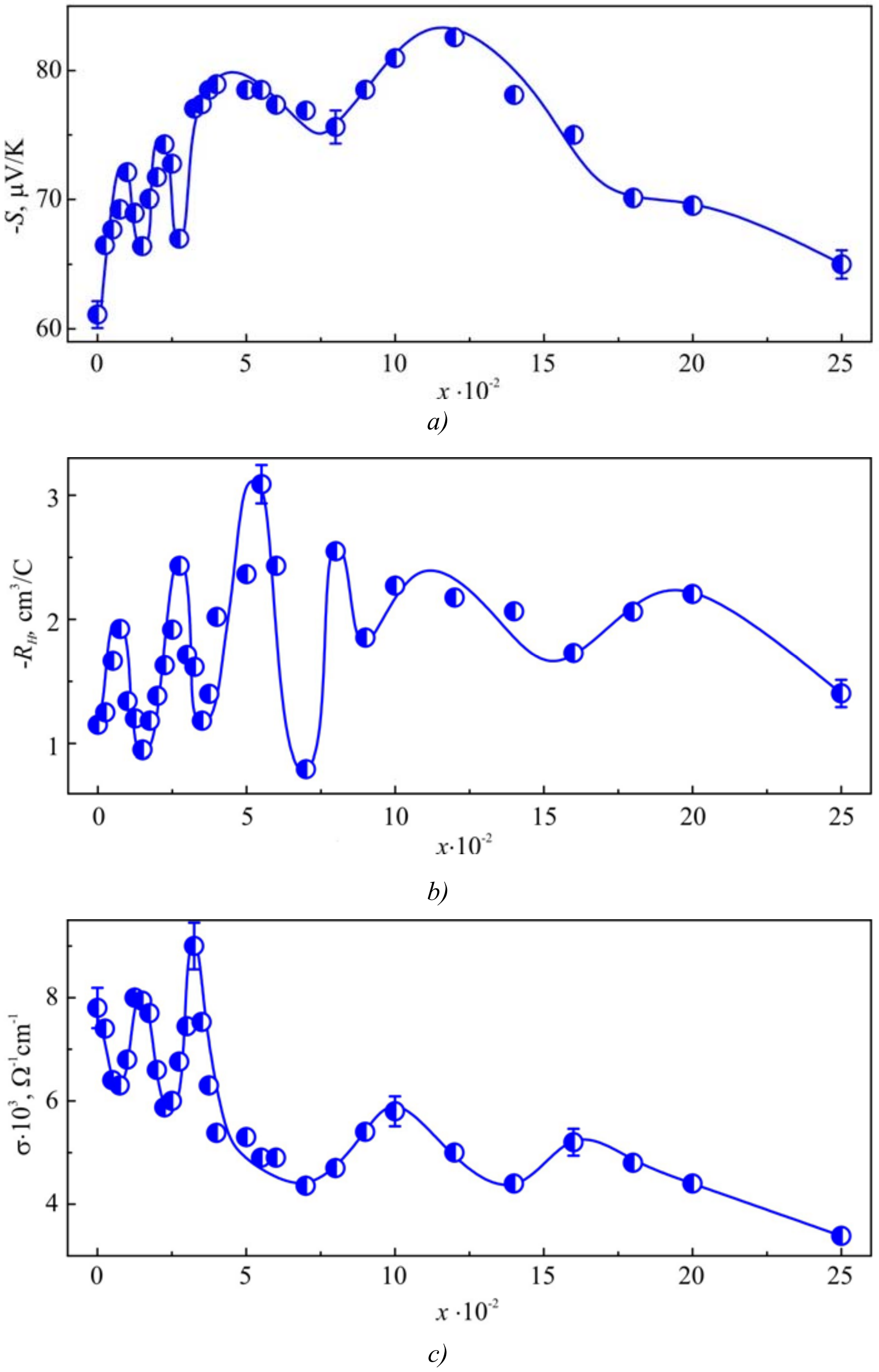

Fig. 2. Dependences of the Seebeck coefficient S (a), the Hall coefficient R_H (b) and electric conductivity σ (c) on the composition x of polycrystalline $Bi_{1-x}Sb_x$ solid solutions at temperature 300 K.

Note first of all the observed similarity between the dependences $S(x)$ and $R_H(x)$. Firstly, up to $x \sim 0.12$, despite the non-monotonic oscillating behaviour of these curves, there is a tendency to growth of S and R_H with increase in x. Secondly, in both cases in the concentration ranges $x = 0.01 \div 0.015$, $x = 0.025 \div 0.035$ and $x \sim 0.05 \div 0.10$ on the dependences $S(x)$ and $R_H(x)$ there is an anomalous reduction of S and R_H with increase in antimony content. We have observed such concentration anomalies earlier [46 – 55] in the investigation of cast $Bi_{1-x}Sb_x$ samples obtained with the use of other kinds of thermal treatment, as well as pressed samples prepared therefrom. We attributed the presence of anomalies to manifestation of critical phenomena accompanying electron phase transitions occurring in $Bi_{1-x}Sb_x$ solid solutions with increase in antimony concentration. Thirdly, positions of maxima and minima on the dependences $S(x)$ and $R_H(x)$ practically coincide for the concentration ranges $x = 0.01 – 0.015$ and $x = 0.025 – 0.035$ (though S and R_H were measured independently), but differ for the range $x \sim 0.05 – 0.10$: on the dependence $R_H(x)$ in the composition range $x = 0.05 – 0.10$ there are two areas of anomalous reduction of R_H in contrast to S, where one minimum is observed close to $x \sim 0.07$.

From the dependence $\sigma(x)$ it is seen (Fig. 2*c*) that over the entire investigated composition range ($x = 0 – 0.25$) with a general non-monotonic behaviour of the curve there is a tendency to electric conductivity drop with increase in x. In the composition area $x = 0 – 0.1$, like in the case of S and R_H, there are concentration anomalies (growth of σ with increase in x), and maxima on the curves S and R_H are matched by minima on the curve $\sigma(x)$, which is easy to explain by different dependence of these kinetic coefficients on charge carrier concentration.

As regards thermal conductivity of $Bi_{1-x}Sb_x$, there is a tendency to reduction of λ with increase in *Sb* concentration to $x \sim 0.16$, following which λ increases slightly (Fig. 3). Like in the case of other kinetic coefficients, on the curve $\lambda(x)$ there are areas of anomalous change (growth) of thermal conductivity with increase in *Sb* concentration, though the anomalies corresponding to transition to gapless state and semimetal-semiconductor transition are not so distinctly divided in concentration, as in the case of curves $\sigma(x)$, $S(x)$ and $R_H(x)$, and partially overlap. It should be also noted that the values of λ obtained here for cast samples practically coincide with the values of λ reported in [52], where λ was measured for pressed samples ($x < 0.1$) prepared prior to pressing by the same technique as cast samples in the present work.

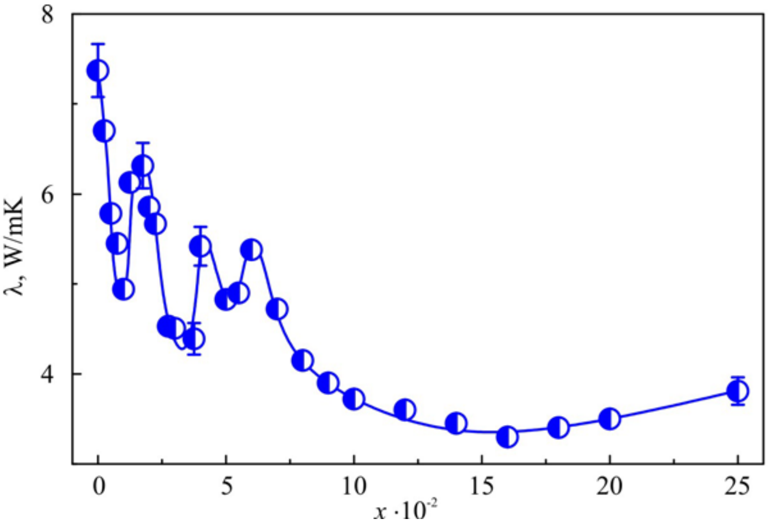

Fig. 3. Dependence of thermal conductivity λ on the composition x of polycrystalline $Bi_{1-x}Sb_x$ solid solutions at temperature 300 K.

At $x > 0.1$ such pronounced extrema on the dependences σ(x), S(x) and R_H(x) are not observed. It can be seen that on the curve S(x) close to composition $x = 0.12$ there is a maximum, following which S is monotonically reduced with increase in x and some inflection in the vicinity of $x = 0.15$. As regards electric conductivity, after the composition $x = 0.1$ the electric conductivity drops to $x \sim 0.14$, then slightly increases to $x \sim 0.16$ and again decreases (Fig. 2*c*). Thus, in the vicinity of composition $x = 0.15$ there are minima on the dependences λ(x) and R_H(x), a maximum on the dependence σ(x) and an inflection on the curve S(x).

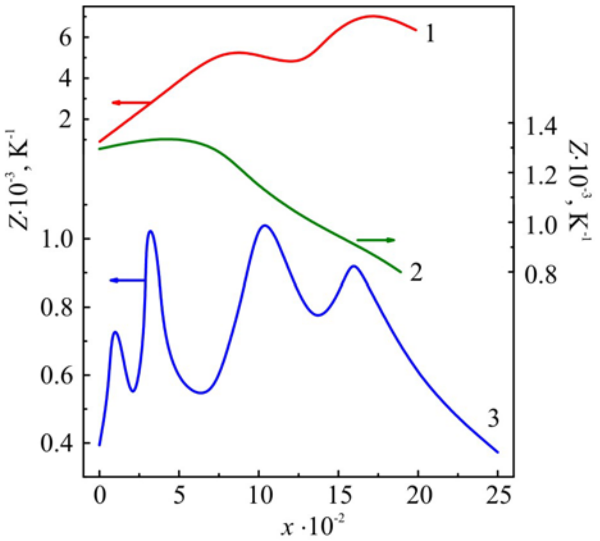

Fig. 4. Dependences of thermoelectric figure of merit Z on the composition x of single crystals (curves 1 and 2) and polycrystals (curve 3) of $Bi_{1-x}Sb_x$ solid solutions at temperatures 300 K (curves 2 and 3) and 60 K (curve 1). Curves 1 u 2 – the results of work [21], curve 3 – the results of the present work.

Based on the resulting values of σ, S and λ, the values of TE figure of merit were calculated. Fig. 4 represents the dependence Z(x) obtained in the present paper for room temperature from which it is seen that in the investigated concentration range on the curve Z(x) one can see four maxima corresponding to compositions $x \cong 0.01$, 0.03, 0.1 and 0.16. Maximum value of Z corresponds to compositions $x = 0.03$ and $x = 0.1$ ($Z = 1.05 \pm 0.05$). For comparison, Fig. 4 shows the dependences Z(x) obtained in [19] for single crystals at temperatures 60 K and 300 K.

Discussion of the results

1. If we mentally draw monotonic components of the dependences S(x), R_H(x), σ(x) and λ(x), it can be said that the dependences S(x) and R_H(x) are curves with a maximum in the vicinity of composition $x = 0.12$, and curves σ(x) and λ(x) show that with a growth of antimony content, σ and λ drop. Such type of the dependence of various properties on the composition of $Bi_{1-x}Sb_x$ solid solutions basically agrees with the data reported in the literature (see above).

As regards the drop of σ and λ with increase in x, similar type of the dependences is typical of solid solutions and can be easily explained by the fact that introduction of impurity component to matrix results in distortions of crystal lattice and chemical bonds and, accordingly, in the emergence of additional centres of electron and phonon scattering, reduction of charge carrier mobility and phonon mean free path length.

On the other hand, with increase in *Sb* content, the value of overlap of the hole *T* and electron L_s bands is reduced, which leads to a reduction of charge carrier concentration, hence, to growth of *S* and R_H. After semimetal-narrow-gap semiconductor transition, growth of energy gap width with increase of *x* to $x \sim 0.12 – 0.15$ also results in the drop of charge carrier concentration, hence, in the growth of *S* and R_H. With increasing concentration $x > 0.12 – 0.15$, the energy gap is reduced, charge carrier concentration grows and a drop of *S* and R_H is observed.

2. Considering the obtained dependences of kinetic coefficients on the composition of $Bi_{1-x}Sb_x$ solid solution in a wide concentration range ($x = 0 – 0.25$) and taking into account our data obtained earlier, it can be seen that the basic difference between these results and the numerous works of other authors studying concentration dependences of properties in $Bi_{1-x}Sb_x$ system is a complicated, oscillating type of dependences $\sigma(x)$, $S(x)$, $R_H(x)$ and $\lambda(x)$ that we noticed for the first time. It was difficult to predict a priori such behaviour of property isotherms with regard to the fact that bismuth and antimony, similar in structure, chemical bond and energy spectrum construction, form a continuous series of solid solutions at all temperatures. Nevertheless, such type of dependences can be explained, at least qualitatively, based on the experimental data, repeatedly confirmed, taking into account the specificity of initial components and the data established today on the character of reconstruction of electron energy spectrum with a change in the composition of $Bi_{1-x}Sb_x$ solid solution. According to [46 – 55], the observed concentration anomalies of kinetic coefficients point to the existence in $Bi_{1-x}Sb_x$ solid solutions at certain *Sb* concentrations of phase transitions accompanied by critical phenomena: percolation-type transition from dilute to concentrated solid solutions, transition to gapless state and semimetal-semiconductor transition.

The type of the dependences $\sigma(x)$, $S(x)$, $R_H(x)$ and $\lambda(x)$ at room temperature in the composition range $x < 0.1$ – the presence of pronounced extrema at certain compositions – coincides with what we have seen earlier [46 – 55] for cast and pressed samples, prepared by different techniques (mainly different time of post-synthesis annealing).

From the obtained results it follows that both a more detailed investigation of the dependences of properties on the composition (the use of a large number of alloys of various composition) and the use of cast polycrystalline samples prepared under strictly identical conditions as the objects of study confirms the presence of three concentration anomalies which we attribute to electronic phase transitions.

However, the presence of a greater number of alloys with different compositions made it possible to discover on the dependence $R_H(x)$, apart from the peak close to $x = 0.06$, an additional peak close to $x = 0.08$, the presence of which can be explained, taking into account the peculiarities of $Bi_{1-x}Sb_x$ band structure and, in particular, the existence of “light” and “heavy” holes (Fig. 1).

Indeed, when with increasing concentration of *Sb* the top of valence *T*-band and the bottom of *L* conduction band are set on the same level, an electronic semimetal-indirect-gap semiconductor transition takes place. With further increase of *x*, as the top of *T*-band drops in energy, the situation is achieved when the top of *T*-band is set on the same level with the top of valence *L*-band, and the semiconductor becomes direct-gap. The character of change in kinetic properties, including thermoelectric, in the area of transition from indirect-gap to direct-gap semiconductor ($x = 0.06 – 0.09$) is rather complicated, being accompanied by a change in the contribution of “light” *L* and “heavy” *T* holes to kinetic coefficients, a change in the energy gap, effective mass, the Hall factor and other parameters. With increase in *x* and further reduction of *T* band in the energy, the contribution to kinetic coefficients of “light” holes increases and the contribution of "heavy" holes decreases. At the same time, the energy gap increases which must lead to a reduction of charge carrier concentration, i.e. to growth of R_H. The influence of these factors on different kinetic coefficients will not be identical. One should also point to strong nonparabolicity of light holes band and the related strong dependence of band parameters at *L*-points of the Brillouin zone on the temperature, composition and technology of samples manufacturing technique. All these peculiarities of $Bi_{1-x}Sb_x$ band structure complicate analysis of transport properties and determination of electronic parameters by the kinetic properties.

The Hall coefficient is very sensitive to a change in the type and concentration of charge carriers. The presence of sharp peaks of R_H at compositions corresponding to system transition to gapless state and semimetal-indirect-gap semiconductor (Fig. 2*b*) testifies to high sensitivity of this kinetic coefficient to qualitative changes in the band structure. Obviously, a change in R_H will not be so considerable, when the band structure does not change so radically, for instance, in the situation when transition from indirect-gap to direct-gap semiconductor occurs, as it takes place at $x \sim 0.08 – 0.09$. The complicated character of dependence $R_H(x)$ in the composition range $x = 0.05 – 0.1$, where we observe two areas of the abnormal reduction of R_H, is attributed to the presence of two electronic transitions in this composition range: a semimetal-indirect-gap semiconductor transition (the energy gap appears between *T* and L_s bands) at $x \sim 0.06 – 0.07$ and an indirect-gap to direct-gap semiconductor transition (the energy gap appears between L_s and L_a gaps) at $x \sim 0.08 – 0.09$ (Fig. 1). On the dependences σ(*x*) and *S*(*x*) these two transitions cannot be "allowed" in concentration in view of lower sensitivity of σ and *S* (as compared to R_H) to changes in the relative contribution of various types of carriers to kinetic coefficients, as well as in view of proximity of concentrations whereby these transitions occur, which leads to overlap of abnormal areas on the dependences σ(*x*) and *S*(*x*) in the concentration range $x = 0.05 – 0.10$.

3. In conformity with the band structure of $Bi_{1-x}Sb_x$ solid solutions at 0 K (Fig. 1), in the range $x = 0.1 \div 0.25$ the presence of peculiarities on the dependences σ(*x*), *S*(*x*), $R_H(x)$ and λ(*x*) might have been expected at critical compositions corresponding to establishment on the same level of the tops of "heavy" *H* and "light" L_s valence bands, when the energy gap is maximal ($x = 0.15 – 0.17$), as to touching the top of "heavy" *H*-band and the bottom of L_a-band (at $x = 0.22$). With a rise in temperature, critical compositions can shift to either side depending on the temperature dependences of kinetic coefficients, the energy gap, effective masses, etc. Based on the obtained dependences σ(*x*), *S*(*x*), $R_H(x)$ and λ(*x*) one can suggest that the anomalies on these curves in the region of compositions close to $x = 0.14 – 0.16$ are related to touching the tops of "heavy" *H* and "light" L_s valence bands, when maximum value of the energy gap is achieved and a transition from direct-gap to indirect-gap semiconductors takes place, with redistribution of charge carriers from L_s valence band to *H*-band. Small number of investigated compositions in the range $x = 0.16 \div 0.25$ does not allow to fix semiconductor-semimetal transition.

4. As mentioned above, the authors of [21, 25] reported on having observed at low temperatures in the undoped $Bi_{1-x}Sb_x$ solid solutions two maxima on the dependence *Z*(*x*) close to compositions $x = 0.09$ and $x = 0.16$, having attributed their presence to the coincidence at above compositions of the extrema of "heavy" *T* and *H* valence bands with the maxima of "light" hole *L* bands. The reduction of *Z* beyond the concentration range $x = 0.09 \div 0.16$ was treated as the result of thermal gap reduction. From the figure given in [21] it is seen that with a rise in temperature to 120 K, on the dependence *Z*(*x*) there is one diffuse maximum close to $x = 0.12$, and at room temperature $Z = 1.3\ 10^{-3}\ K^{-1}$ up to $x \sim 0.07$, and then with increase in *x* it is reduced to $Z = 0.8\ 10^{-3}\ K^{-1}$ at $x = 0.2$.

The authors of [21, 25] surmised that in the range $x = 0.09 \div 0.16$ the top of the valence band consists of "light" mobile holes the presence of which has a negative influence on the value of Z. As long as "heavy" holes corresponding to additional band maxima have considerably lower mobilities, approach of one of these maxima to the main L-extremum reduces the concentration of "light" holes, increasing simultaneously electron concentration. If concentration is not optimal, it may result in Z increase. On the other hand, another factor contributing to growth of Z can be interband scattering due to transitions between the bands of "light" and "heavy" holes that can reduce considerably the mobility of "light" holes and, consequently, increase Z in *n*-type semiconductors. According to the authors of [21, 25], the minimum between two maxima close to compositions $x = 0.09$ and $x = 0.16$ can disappear at higher temperatures, as long as with a rise in temperature the value of kT quickly approaches the value of energy gap between two valence bands.

However, as it follows from Fig. 4, we managed even at room temperature to reveal on the dependence $Z(x)$ four maxima close to compositions corresponding to $x = 0.01$, 0.03, 0.1 and 0.16. The authors of [21, 25] reported only on the presence of the two last extrema that had been observed by them only at low temperatures. Note also that the values of Z obtained in our paper for cast polycrystalline samples and corresponding to extrema close to compositions $x = 0.1$ and 0.16 practically coincide with the values of Z obtained by the authors of [21, 25] for single-crystal samples at room temperature.

Conclusion

A detailed investigation was performed at room temperature of the concentration dependences of galvanomagnetic and TE properties of polycrystalline cast $Bi_{1-x}Sb_x$ ($x = 0 – 0.25$) samples prepared by melt quenching in the air and subsequent homogenizing annealing for 720 hours at temperature (520 ± 5) K. The analysis of the results allowed formulating the following conclusions.

1. The presence of anomalies was confirmed on the dependences of electric conductivity, the Seebeck coefficient, the Hall coefficient and thermal conductivity on the composition of $Bi_{1-x}Sb_x$ alloys that we had observed earlier close to $x = 0.01$; $x = 0.03$ and $x = 0.07$ on the cast samples after different kinds of thermal treatment and on pressed samples, and was attributable to manifestation of critical phenomena at phase transition of percolation type, transition to gapless state and semimetal-semiconductor transition, respectively.
2. For the first time the complicated type of dependence $R_H(x)$ was revealed in the composition range $x = 0.05 – 0.1$, manifested in the presence of two areas of abnormal reduction of R_H. The observed effect is interpreted as a consecutive manifestation of semimetal-indirect-gap semiconductor and indirect-gap semiconductor-direct-gap semiconductor transitions.
3. It was shown that at $x > 0.1$ the concentration dependences of properties are also of non-monotonic nature. The complicated type of dependences at $x > 0.1$ is attributable to qualitative changes in the structure of $Bi_{1-x}Sb_x$ energy spectrum at certain critical compositions, a change in the relative contribution to conductivity of charge carriers from various energy bands with a change in antimony concentration, as well as to high sensitivity of electron spectrum and physical properties of $Bi_{1-x}Sb_x$ to external effects.
4. On the dependence of TE figure of merit Z on the composition of $Bi_{1-x}Sb_x$ solid solutions at room temperature there were revealed four maxima close to compositions corresponding to $x = 0.01$, 0.03, 0.1 and 0.16. The presence of extrema on the curve $Z(x)$ is related to qualitative

changes in the energy spectrum of charge carriers at some critical compositions in $Bi_{1-x}Sb_x$ system determining the existence of electron concentration phase transitions accompanied by critical phenomena.

5. It was shown that at room temperature on the cast polycrystalline samples prepared by quenching in the air and subsequent annealing for 720 hours at (520 ± 10) K one can achieve the values of TE figure of merit Z that are not inferior to the values of Z obtained on polycrystals subject to a longer annealing, as well as on single-crystal samples.

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