Effect of sample preparation method on the manifestation of percolation phenomena in the thermoelectric properties of $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions in the range $x = 0.93-1.00$

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The purpose of the present work was to find out how the method of sample preparation influences the character of the manifestation of the percolation transition. We obtained the room temperature dependences of electrical conductivity, the Seebeck coefficient, and the TE power factor on the composition of $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions ($x = 1-0.93$) for samples pressing and subjected to long-term aging and ones prepared by other methods. The percolation effects were observed for all samples irrespective of the preparation technique, although the concentration region and the character of their manifestation differed from what we observed earlier for rapidly cooled cast alloys. In addition, in the aged samples, one more peak at $x \sim 0.965$ was detected and attributed to the processes of self-organization in the solid solution occurring after reaching the percolation threshold.

Keywords: $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions; composition, aging, pressing, electrical conductivity, Seebeck coefficient, thermoelectric power factor, percolation, phase transition, self-organization.

Вплив методу приготування зразків на прояв перколяційних явищ у термоелектричних властивостях твердих розчинів $(Bi_{1-x}Sb_x)_2Te_3$ в діапазоні $x = 0.93-1.00$. *О.І.Рогачова, К.В.Мартинова, О.М.Нащекіна, В.Є.Марценюк*

Мета роботи — з'ясувати, як спосіб приготування зразків впливає на характер прояву перколяційного переходу. Одержано залежності електропровідності, коефіцієнта Зеєбека та ТЕ потужності від складу сплавів $(Bi_{1-x}Sb_x)_2Te_3$ ($x = 1-0,93$) після використання різних швидкостей охолодження зразків після високотемпературного відпалу, тривалого (протягом 5 років) старіння при кімнатній температурі та пресування. Встановлено, що перколяційні ефекти спостерігаються для всіх використаних методів приготування зразків, хоча концентраційний інтервал їх прояву дещо зміщений у бік збільшення вмісту Bi у порівнянні із швидко охолодженими сплавами. Крім того, у зістарених зразках спостерігається ще одна концентраційна аномалія при більшому вмісті Bi, наявність якої ми пов'язуємо зі процесами самоорганізації твердого розчину, що відбуваються після досягнення порогу перколяції.

1. Introduction

The thermoelectric (TE) method of direct energy conversion (heat — electricity or electricity — heat) attracts increasing attention of researchers and practitioners due to a number of advantages it has over traditional methods of generating energy and cooling. This determines the need to develop high-efficiency materials for TE converters. The efficiency and therefore the quality of a TE material is characterized by the quality index of TE: $Z = S^2\sigma/\lambda$ (S is the Seebeck

coefficient, σ is the electrical conductivity, and λ is the thermal conductivity) [1–3]. One of the well-known and traditional methods for increasing Z is the so-called "solid solution method", and the most promising TE materials are solid solutions. This necessitates a detailed study of the dependences of the properties of solid solutions on the concentration of the introduced component. On the one hand, such studies should be conducted in a wide range of concentrations, since a significant decrease in λ is usually observed when a large amount of the second component is introduced. On the other hand, when using doping for optimizing the TE properties of a compound or solid solution, it is important to carry out a detailed investigation in a narrow range of compositions.

When the "solid solution method" is applied, it is conventionally assumed that the properties of a solid solution change monotonically and continuously with composition as in an ideal solid solution. However, the results of some studies contradict these simplified assumptions. In a number of our works, we observed concentration-dependent anomalies of properties in the region of low impurity content (see, e.g., [4–6]). We related them to the percolation phenomena [7, 8] in a solid solution and assumed that such phenomena take place in any solid solution. The situation becomes more complicated when the interaction is not between pure elements (e.g., Bi and Sb) but between chemical compounds, which is common in TE materials science. In this case, the associated solid solutions can be formed with a high probability, in which clusters (associates) rather than individual impurity atoms should be considered as structural components. The chemical composition of such clusters corresponds most likely to the composition of the introduced compound (especially, if a stable congruently melting compound is introduced) [9, 10].

It should also be noted that TE converters often use polycrystalline, in particular, pressed materials. Although single-crystalline samples usually have higher maximum Z values than polycrystalline ones, single crystals are rarely used in the mass production of TE legs due to the high cost and low mechanical strength of these materials. For a large-scale production of legs from TE alloys, powder metallurgy methods are used. Therefore, the study of the properties of pressed materials is of particular interest.

An important characteristic of any device is the service life, i.e. the time during which the device remains functional. The service life of a TE device is very high compared to other power generators or cooling devices due to its solid construction; however, it largely depends on the properties of the TE material. Therefore, one of the key characteristics of a TE material is its service life in devices.

Among the best materials that are used to produce TE refrigerators are those based on V_2VI_3 semiconductors, including $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions of Bi_2Te_3 and Sb_2Te_3 compounds. Basic information about the structure and electronic properties of these compounds and their solid solutions is given in [1–3, 11]. In [12], the results of our study of the properties of cast and cold-pressed samples of $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions in the entire concentration range ($x = 0$–1) showed that in pressed samples near the composition $x = 0.8$, high values of Z are achieved, comparable to those reported for single-crystalline and hot-pressed samples. In cast samples of the same solid solutions, in the range $x = 0$–0.07, we found concentration-dependent anomalies of mechanical, galvanomagnetic and TE properties and attributed them to percolation effects in solid solutions [13, 14]. We observed similar non-monotonic dependences of the properties on composition in the range $x = 0.93$–1.0 (at a low Bi content) in cast alloys $(Bi_{1-x}Sb_x)_2Te_3$ annealed at high temperature and then rapidly cooled to room temperature, and explained this phenomenon by the manifestation of the percolation transition (PT) [15]. The question arises about the stability of the percolation phenomenon and influence of different factors on the character of its manifestation.

The purpose of this work was to study the influence of the sample preparation method (casting or pressing), heat treatment, and long-term aging on the manifestation of percolation effects in $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions in the concentration range $x = 0.93$–1.0.

2. Experimental

All 20 polycrystalline $(Bi_{1-x}Sb_x)_2Te_3$ samples with different compositions in the range $x = 1.0$–0.93 were synthesized and subjected to heat treatment in one technological cycle ensure their complete identity. The samples were obtained by fusing high-purity elements (99.999 % of the main component) in evacuated to 10^{-3} Pa quartz am-

poules at (1020 ± 10) K for 5 hours using vibrational mixing, subsequent cooling down to the temperature of (650 ± 10) K, at which the alloys solidified, and holding at this temperature for 300 hours.

After that, the ampoules with samples were cooled in air; the dependences of mechanical, electrophysical, galvanomagnetic and TE properties on the composition were measured and the results obtained are described in detail in [15]. Let's denote this method of sample preparation as T1.

A part of each sample was crushed to obtain powder with a dispersion of ~ 200 μm, which was then subjected to cold pressing at room temperature (load 7 t/cm^2, holding time under pressure is 1 min). The pressed samples were cylinder-shaped with a diameter $d = 15$ mm and a height $h = 5$ mm. After that, the obtained pressed samples were annealed in evacuated to 10^{-3} Pa glass ampoules at 690 K for 300 h and then cooled down to room temperature in the switched off furnace at a rate of ~ 20 K/hour. We designated this method of preparing samples as T2.

The remaining parts of each sample, after being quenched in air, were placed in bags to prevent the direct contact with air and aged at room temperature for 5 years (method T3).

The following method of the sample treatment T4 we used to observe the percolation effects. After the long-term aging (T3), the electrical conductivity σ of some samples was measured in the temperature range 77–300 K; the samples were placed in liquid nitrogen, then slowly heated to room temperature and after that σ was measured to see the possible effect of exposing the samples to low temperatures. The methods for determining chemical composition, microstructure, crystal structure, microhardness and measuring electrical conductivity σ and the Seebeck coefficient S were described in our previous works [12–15].

3. Results and discussion

Figs. 1, a–d show the dependences of electrical conductivity σ on composition of the $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions in the range $x = 1.0$–0.93 for different methods of samples preparation and treatment (T1–T4).

It can be seen (Fig. 1, a) that in the T1 mode [15], the introduction of the first portions of Bi (up to $x = 0.995$) leads to a sharp decrease in σ, a sharp increase in σ at $x = 0.9925$ and the subsequent decrease. As

a result, in the σ(x) dependence, a narrow sharp peak is observed, which we attribute to the existence of the percolation transition [15].

In Fig. 1, b, the σ(x) dependence for the pressed samples prepared by the T2 method is shown. First, σ decreases, then at $x = 0.99$, it starts increasing. It grows up to the concentration $x \sim 0.985$ and then decreases. The corresponding maximum in the σ(x) curve indicates the presence of a phase transition. This maximum is not as sharp as that for the sample cooled in air (T1). Besides, there is an inflection in the σ(x) dependence near $x = 0.97$, moreover, the behavior of the σ(x) curve after the maximum differs qualitatively from the behavior of the dependence σ(x) for the samples prepared by T1. One can also see that the values of σ are lower after pressing.

The σ(x) curve for the samples aged for 5 years at room temperature (T3) shows two distinct maxima near $x = 0.985$ and $x = 0.965$ (Fig. 1, c). The position of the second maximum is close to the position of the inflection in the σ(x) curve for the pressed samples annealed at 690 K and then slowly cooled to room temperature (T2).

As noted above, in the T4 treatment mode, before measuring σ at room temperature, the samples aged according T3 were placed into liquid nitrogen and then slowly heated from 77 K to 300 K. As the measurements were not carried out for all samples, it was impossible to plot a detailed σ(x) dependences as for the aged samples, which were not cooled and heated before measuring σ. Despite that, the σ(x) curves for the samples treated in the T4 mode have the main features of similar dependences for other methods of sample preparation, namely, the presence of a phase transition, which we interpret as a percolation type phase transition.

Fig. 2 shows the dependences of the Seebeck coefficient (Fig. 2, a–c) and TE power factor $P = S^2 \cdot \sigma$ (Fig. 2, d–f) on composition of the $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions in the region $x = 1.0$–0.93 for different modes of samples preparation (T1–T3). The $S(x)$ dependences exhibit concentration anomalies in the same concentration ranges as on the σ(x) curves, which we associate with the manifestation of the percolation transition. However, for the pressed samples, we did not observe such a sharp change in S in the region of the percolation transition as in
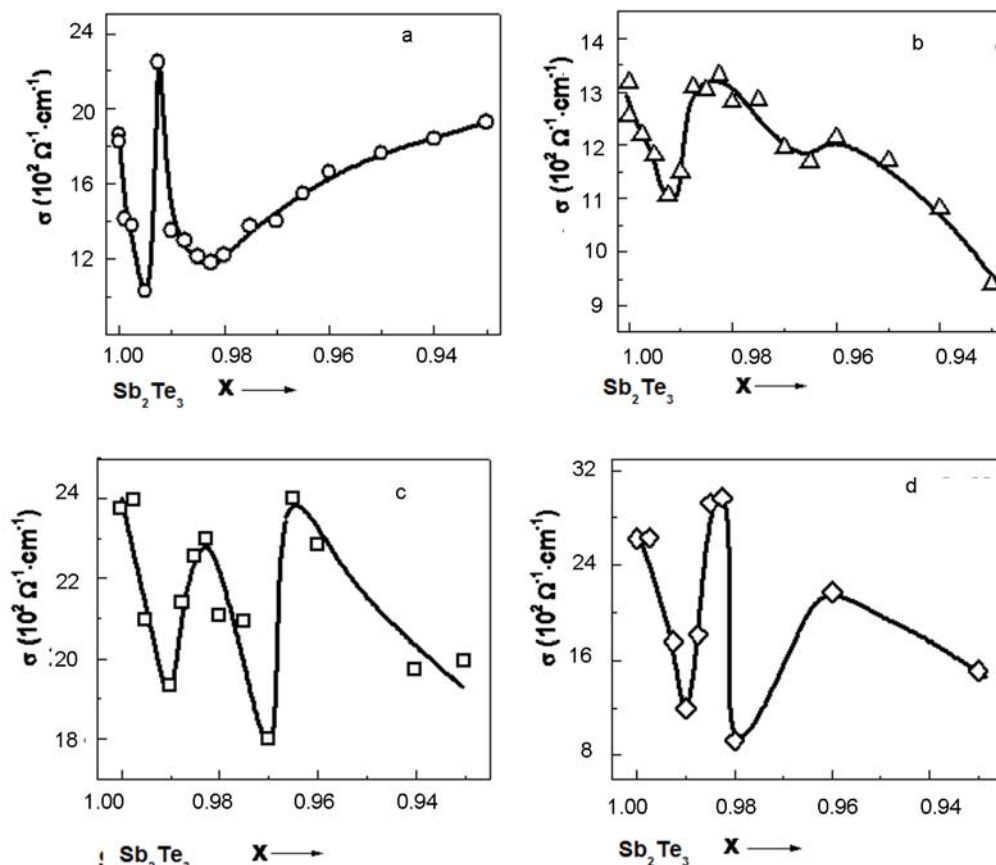
Fig. 1. Room-temperature dependences of electrical conductivity σ on composition x for the $(Bi_{1-x}Sb_x)_2Te_3$ solid solution samples subjected to different methods of treatment: a) cooling in air after annealing at 650 K for 300 h (T1); b) cold-pressing with subsequent annealing at 690 K for 300 h and slow cooling down to room temperature in the switched off furnace (T2); c) long-term aging for 5 years (T3) at room temperature; d) subjecting the aged samples to cooling down to 77 K and subsequent heating up to 300 K (during measurements).

the case of electrical conductivity: while σ increases noticeably, S remains almost constant.

In addition, for the pressed samples, we were unable to discern any inflections near $x = 0.965$ in the $\sigma(x)$ dependences. However, for the cast samples "aged" at room temperature for 5 years, both the $\sigma(x)$ and $S(x)$ dependences exhibited two distinct extrema (a maximum for σ and a minima for S) near $x = 0.985$ and $x = 0.96$.

Comparative analysis of the TE power factor P dependences on composition in the range $x = 0.93-1.0$ for the samples prepared by different methods shows that the dependences are non-monotonic, due to the non-monotonic character of the concentration dependences of S and σ. However, P changes in a rather narrow range of values, and the maximum values do not exceed $17 \cdot 10^{-4}$ W/m·K^2.

Thus, the analysis of the experimental results shows that for all applied methods of sample preparation and treatment, a phase transition is observed; we attribute it to the reaching of the percolation threshold and the formation of the so-called infinite cluster. In other words, this abrupt change in σ and S at a certain composition is not a result of some specific phenomena caused by the sample preparation method, for example, a martensitic-type phase transition. Also, the change in the properties does not indicate a nonequilibrium phase transition, since it is observed even in the samples kept at room temperature for 5 years.

The shift in the percolation threshold towards a lower Bi concentration for samples prepared in the T1 mode can presumably be explained as follows. Rapid cooling after high-temperature annealing leads to strong lattice instability associated with the appearance of quenching-induced defects
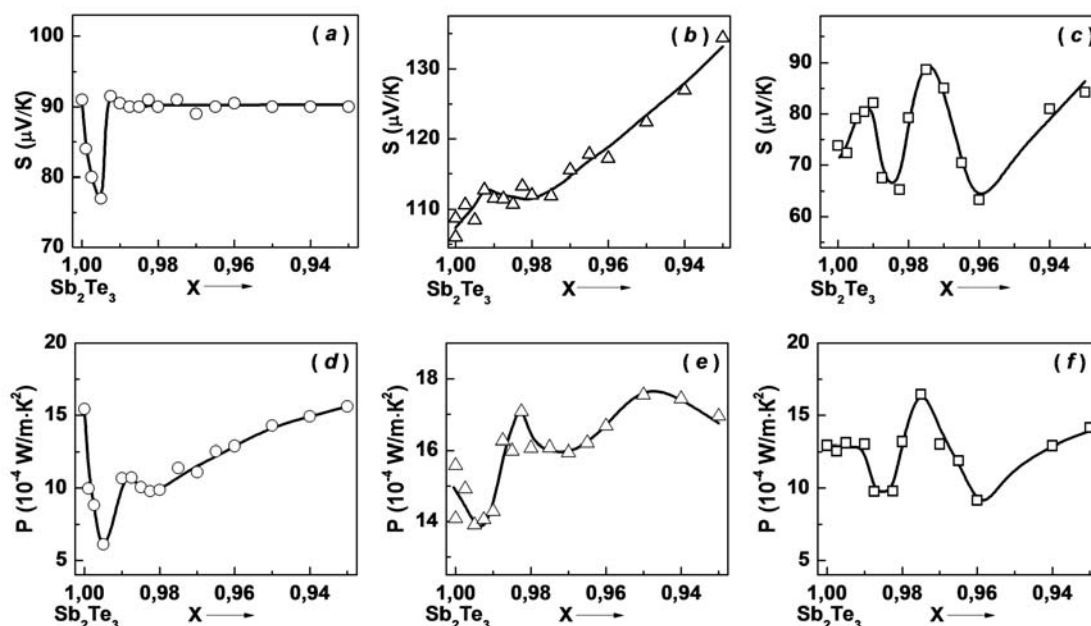
Fig. 2. Room-temperature dependences of the Seebeck coefficient S (a, b, c) and TE power factor $P = S^2 \cdot \sigma$ (d, e, f) on composition x for the $(Bi_{1-x}Sb_x)_2Te_3$ solid solution samples processed in different modes: a, d) cooling in air after annealing at 650 K for 300 h (T1); b, e) cold-pressing with subsequent annealing at 690 K for 300 h and slow cooling down to room temperature in the switched off furnace (T2); c, f) long-term aging for 5 years (T3) at room temperature.

which are nonequilibrium at room temperature. These defects explain the observed increase in the hole concentration upon the introduction of the first portions of the impurity component (Bi) [15]. As a result, the percolation transition occurs against the background of an increased concentration of holes, and this in turn determines the observed shift of the percolation threshold towards lower values of x. The existence of nonequilibrium states and relaxation phenomena leading to a more distinct manifestation of the existing phase transition is similar to the crystallization of a supercooled liquid or the heating of an amorphous phase capable of crystallizing. The lattice instability also leads to an increase in σ in the region $x > 0.98$, which is inconsistent with the commonly observed dependence in this system.

After slow cooling of the pressed samples (T2), the percolation transition manifests itself through a clearly pronounced, but rather wide maximum in the $\sigma(x)$ dependence and a sharp change in the character of the $S(x)$ dependence (a distinct increase in S is followed by its practical constancy in the composition range $x = 0.995-0.97$). At the same time, σ decreases with increasing Bi concentration (decreasing x) in the region x

> 0.98; this corresponds to the dependence usually observed for this system in an equilibrium state, which indicates that the system has reached an equilibrium state. The inflection in the $\sigma(x)$ dependence near $x = 0.97$ indicates the possibility of some phase transformations in the solid state.

The long-term aging of the samples for 5 years (T3) led to the appearance of two clearly visible extrema both on the $\sigma(x)$ and $S(x)$ dependences. We attribute one of them to the percolation transition, and the other to the phase transformation in the solid state that becomes possible only after reaching the percolation threshold when the interaction of impurity atoms in the solid solution becomes cooperative. It can also be suggested that the second peak is associated with another percolation transition, when a transition to an associated solid solution occurs, i.e. a continuous chain of interactions is formed not between individual Bi impurity atoms, but between Bi_2Te_3 associates. The appearance of such a continuous chain of interactions between associates can stimulate the processes of both short- and long-range ordering with a high probability.

From the analysis of the data obtained for the samples prepared and treated in the T4 mode, it can be assumed that due to a

sharp decrease in the temperature of the samples immersed in liquid nitrogen, the crystal is oversaturated with defects; their concentration exceeds the equilibrium one, the redistribution of the defects is not completed, and ordered configurations corresponding to low temperatures are not formed. During subsequent heating to room temperature, on the one hand, the transition to the equilibrium state takes place, the diffusion rate increases and the system approaches the equilibrium. On the other hand, phase transitions can take place.

For the pressed samples in the range $x = 0.985-0.93$, TE power factor P practically does not change with composition, reaching the value $P = (17-18){\cdot}10^{-4}$ W/m·K^2. However, after aging, the maximum value of P is observed only for $x = 0.97$; it sharply decreases to $P = 10{\cdot}10^{-4}$ m·K^2 with the deviation from this composition. Thus, self-organization processes in solid solutions, whose manifestation becomes pronounced only after long aging, should be taken into account when interpreting and predicting the properties of TE solid solutions.

In conclusion, we would like to note that the results obtained in this work are important from the point of view of doping individual compounds or solid solutions to obtain optimal charge carrier concentrations. Usually, no more than 1–2 % of impurity is introduced through doping, and this is the concentration range in which percolation effects manifest themselves. So, their presence should always be foreseen and taken into account.

4. Conclusions

The room-temperature dependences of electrical conductivity, the Seebeck coefficient, and TE power factor on the composition of $(Bi_{1-x}Sb_x)_2Te_3$ ($x = 1-0.93$) alloys were measured for samples processed in different modes: hardening from high temperatures, heating from low temperatures, pressing, and long-term aging.

It has been established that percolation effects are observed for all sample preparation modes. The position of the peak corresponding to the percolation phase transition ($x \sim 0.985$) does not depend on the treatment mode, except for the case when the sample is rapidly cooled from a high temperature ($T = 650$ K) to room temperature,

then the peak position shifts to $x = 0.995$. The shape, width, and height of the peak change with changing in the sample preparation mode.

For the long-term aged samples, an additional concentration-dependent anomaly is observed in the $\sigma(x)$ and $S(x)$ curves at a Bi concentration higher than the percolation threshold. We attribute its presence to the processes of self-organization in the solid solution after reaching the percolation threshold.

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