Percolation effects in semiconductor $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions at small Bi concentration

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Polycrystalline samples of semiconductor $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions in the range of compositions $x = 1 - 0.93$ were synthesized. The dependences of microhardness, electrical conductivity, the Hall coefficient, the Seebeck coefficient, concentration and mobility of charge carriers on the solid solution composition x were obtained at room temperature. It was established that in these dependences, concentration anomalies are observed in the same range of compositions ($x = 0.995 - 0.98$) for different properties, which indicates the presence of a phase transition. It is assumed that this phase transition has a percolation nature and indicates that at a certain concentration of the impurity component (Bi) a continuous chain of interacting impurity atoms that permeates the crystal (an infinite cluster) is formed, and then the interaction becomes collective. These results are another confirmation of our earlier stated assumption that this phenomenon is universal for all solid solutions, and its existence should be taken into account when developing and interpreting the properties of materials.

Keywords: $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions; composition; microhardness; electrical conductivity; Hall coefficient; Seebeck coefficient; charge carrier mobility; percolation; phase transition

Перколяційні ефекти у напівпровідникових твердих розчинах $(Bi_{1-x}Sb_x)_2Te_3$ при малих концентраціях Bi. *О.І.Рогачова, К.В.Мартинова, О.М.Нащекіна, Ю.В.Меньшов*

Виготовлені полікристалічні зразки напівпровідникових твердих розчинів $(Bi_{1-x}Sb_x)_2Te_3$ в інтервалі складів $x = 1.00 - 0.93$. Одержано залежності мікротвердості, електропровідності, коефіцієнта Холла, коефіцієнта Зеєбека, концентрації та рухливості носіїв заряду від складу x твердого розчину при кімнатній температурі. Встановлено, що на цих залежностях спостерігаються концентраційні аномалії в одному і тому ж для різних властивостей інтервалі складів: $x = 0.995 - 0.98$, що свідчить про наявність фазового переходу. Висловлено припущення, що цей фазовий перехід має перколяційну природу і свідчить про створення при певній концентрації домішкового компонента (Bi) безперервного ланцюжка взаємодіючих домішкових атомів, що пронизує кристал (нескінченного кластера), після чого взаємодія набуває колективного характеру. Ці результати є ще одним підтвердженням висловленого нами раніше припущення про універсальний характер цього явища, притаманного всім твердим розчинам, наявність якого слід враховувати при розробці і інтерпретації властивостей матеріалів.

1. Introduction

One of the main methods for controlling properties of semiconductor materials is the introduction of additional components into them. That is why most of the materials used in practice are solid solutions with a certain concentration of a new component introduced into the original crystal. If the amount of this component does not exceed (1–2)%, then we talk about doping.

The main task of thermoelectric (TE) materials science is to find methods for increasing the figure of merit of materials $Z = S^2\sigma/\lambda$ (S is the Seebeck coefficient, σ is the electrical conductivity, λ is the thermal conductivity), which largely determines the efficiency of a TE generator or cooling device [1-3]. The traditional method for solving this problem consists in the formation of an isovalent solid solution to reduce the lattice thermal conductivity and its subsequent doping to obtain the required type of conductivity and the optimal concentration of charge carriers. It defines the need to know the region of existence of a solid solution and the dependences of properties on the concentration of the introduced components.

According to the ideal solid solution model which assumes a random distribution of non-interacting with each other atoms of the introduced component and the additivity of the thermodynamic characteristics, the properties of solid solution should change monotonically and continuously with changing composition [4]. In an ideal solid solution, the configurational entropy S increases and the Gibbs free energy decreases, which corresponds to the spontaneity of the mixing process. In a more rigorous model of regular solid solution, the distribution of atoms is also considered random, the S value coincides with that for an ideal solid solution, the interaction energy between atoms does not depend on the composition and cannot affect their distribution. While ideal solutions can be described by their thermodynamic functions through the properties of the components, and regular solutions can be described using the interaction energy, then real solutions require experimentally determined values of excess thermodynamic functions or so-called activity coefficients. But none of these approximations indicated the possibility of percolation phenomena [5,6] in a solid solution, which could affect the character of the composition dependences of properties.

However, the authors of a large number of works have observed in a number of solid solutions based on IV-VI, V_2VI_3 compounds, and other solid solutions, clearly expressed concentration anomalies of properties in the region of low impurity atoms (IAs) concentrations (see, for example, [7-10]) and suggested the universality of the observed phenomenon which has a percolation nature [11-13] and inherent in any solid solution. To confirm this assumption and establish general patterns regarding the critical concentration (percolation threshold), the nature of the manifestation of the percolation effect depending on the chemical nature of the components, temperature, sample preparation technology, etc., it is necessary to expand both the range of objects and the range of properties under study.

The objects of study in this work are the $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions formed between the Bi_2Te_3 and Sb_2Te_3 compounds, which crystallize like the initial components in a rhombohedral structure of the tetradymite type and are currently among the most efficient TE materials used in the creation of devices for TE cooling at temperatures near room temperature [1-3,14]. Studies of the TE properties of the Sb-Bi-Te system along the $Bi_2Te_3 - Sb_2Te_3$ section were carried out by many authors (see, for example, [14-21]). However, in almost all works, the samples were made with a large concentration step. As far as we know, only in [22] the dependences of TE properties on the composition were studied with a small step in concentration in $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions near Bi_2Te_3 ($x = 0 - 0.07$) at room temperature and for all properties, these dependences showed peaks in the composition range $x = 0.01 - 0.015$. These concentration anomalies were attributed by the authors of [22] to the formation of percolation channels through Sb atoms at a critical concentration corresponding to the percolation threshold x_c [5,6]. It could be expected that a similar situation would also be observed in this system for Sb_2Te_3-based solid solutions, which, however, required experimental verification and was the subject of research in the present work.

It should be added that when using materials in TE devices, certain requirements are imposed not only on TE, but also on other properties that determine their possibility of practical use, including mechanical properties. One of the informative mechanical characteristics is microhardness H, which characterizes the strength during the penetration of an indenter [23] and is related to other mechanical characteristics by certain relationships. Therefore, it was also of interest to study the dependence of H on the composition in the $(Bi_{1-x}Sb_x)_2Te_3$ solid solution.

The purpose of this work is to obtain the dependences of H, galvanomagnetic and TE properties of $(Bi_{1-x}Sb_x)_2Te_3$ on the composition in the range $x = 0.93 - 1.0$, corresponding to a low content of Bi, to identify the percolation transition and its effect on the properties.

As a result of the studies, it was found that in the $(Bi_{1-x}Sb_x)_2Te_3$ system in a narrow concentration range $x = 0.995 - 0.98$, all dependences show clearly pronounced anomalies, which most likely correspond to the percolation transition from an impurity discontinuum to an impurity continuum.

2. Experimental

Polycrystalline samples of $(Bi_{1-x}Sb_x)_2Te_3$ ($x = 1.0 − 0.93$) were obtained from high-purity elements (99.999% of the main component) by their fusion in evacuated to 10^{-3} Pa quartz ampoules at temperature (1020 ± 10) K for 5 hours using vibrational mixing, subsequent cooling to a temperature of (650 ± 10) K, when the alloys passed into the solid state, holding at this temperature for 300 hours, after which the ampoules with samples were cooled in air. All 20 samples of different compositions were prepared simultaneously, in one technological cycle, which ensured the identity of the conditions for their preparation.

Determination of the chemical composition of the obtained samples by X-ray fluorescence and electron probe analysis showed that the deviation from the specified composition for all elements did not exceed $\Delta x = 0.0002$. H was measured using PMT-3 device with a diamond pyramid. The choice of the load on the indenter (P) was carried out by plotting the dependences $H(P)$ for each sample and determining the $P=P_c$ value, after which H ceased to depend on P and became an objective characteristic of the strength properties. It was found that with P increasing, H decreases, that is, there is a so-called "scale effect" and $P_c = 0.49$ N. The value of H for each sample was obtained as the mean value when measuring 30 prints, and the statistical processing of the experimental results showed that the relative root-mean-square fluctuation of H did not exceed 2–3%. Measurement of galvanomagnetic and TE properties was carried out on samples in the form of parallelepipeds, cut from the obtained cast samples. The determination of σ and the Hall coefficient R_H with an accuracy of not less than $\pm$ 5% was carried out using the Van der Pauw method at a magnetic field induction $B = 1$ T. The Seebeck coefficient S was measured by the compensation method with respect to Cu electrodes with an error of $\pm$ 3%. In accordance with R_H and S measurements, all obtained samples had p-type conductivity. The Hall concentration of charge carriers (holes) p_H was calculated by the formula $p_H = r/(e \cdot R_H)$, assuming that the Hall factor is $r = 1$, and the Hall mobility μ_H was determined as $\mu_H = R_H \sigma$. The value of TE power factor P was estimated by the formula $P = S^2\sigma$. All measurements were carried out at room temperature.

3. Results

In Fig. 1, a, the $H(x)$ dependence for $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions in the concentration range $x = 1.0 − 0.93$ is shown. When the first portions of Bi_2Te_3 are introduced into Sb_2Te_3

($x = 1.0$) up to $x = 0.995$, a sharp (by a factor of ~1.7) increase in H is observed, however, with a further increase in the Bi content (decrease in x), H sharply drops to $x = 0.9875$, after which it remains unchanged.

The dependences $\sigma(x)$, $R_H(x)$, $\mu_H(x)$, and $S(x)$ also have a clearly pronounced nonmonotonic character (Fig. 1, b-e). The values of σ, R_H, μ_H, and S ($\sigma = 1865$ Ом$^{-1} \cdot$см^1, $R_H = 0.05$ см^3/K, $\mu_H = 100$ cm^2/(V ·s) and $S = 91 \mu$V/K) obtained for the stoichiometric Sb_2Te_3 are in good agreement with the data of other authors for cast polycrystalline samples of Sb_2Te_3. With the introduction of the first portions of Bi_2Te_3 into Sb_2Te_3 in the range $x = 1.0 − 0.995$, σ, R_H and μ_H sharply decrease, then in the range $x = 0.995 \div 0.9925$ their rapid growth and subsequent decrease in the range $x = 0.9925$-0.98 are observed, after which σ and μ_H increase monotonically up to $x = 0.93$, while the R_H value (and, accordingly, the hole concentration) remain almost unchanged. Thus, the dependences $\sigma(x)$, $R_H(x)$, and $\mu_H(x)$ show maxima (especially sharp for σ and μ_H) near $x = 0.9975$ and two minima near $x = 0.995$ and $x = 0.9825$. In the $S(x)$ dependence, one can see a clearly pronounced minimum near $x = 0.995$, as well as on the dependences $\sigma(x)$, $R_H(x)$ and $\mu_H(x)$.

Based on the values of R_H under the assumption of one type of charge carriers, the Hall concentration of holes p_H was calculated. The dependence $p_H(x)$ is shown in the inset to Fig. 1, c. With the introduction of the first portions of Bi_2Te_3 in the range $x = 1 − 0.995$, the p_H value increases sharply from $p_H = 1$ 10^{20} см$^{-3}$ до $p_H = 3.5$ 10^{20} см$^{-3}$, then it also sharply drops to almost the original value, after which it again slightly increases, remaining starting from $x = 0.98$, almost unchanged.

It can be seen from Fig. 1, f that the presence of concentration anomalies in the dependences $\sigma(x)$ and $S(x)$ leads to a decrease in the TE power factor $P = S^2\sigma$ upon the introduction of Bi_2Te_3 into Sb_2Te_3 down to $x \sim 0.98$. Even with a subsequent increase in P up to $x = 0.93$, the value of P reaches only the value inherent in Sb_2Te_3.

4. Discussion

Thus, the character of the dependences of mechanical, galvanomagnetic and TE properties on the composition of $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions between Sb_2Te_3 and Bi_2Te_3 semiconductor compounds indicates qualitative changes in the lattice and electronic subsystems of the crystal with increasing Bi_2Te_3 concentration and the presence of a phase transformation. Meanwhile, the $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions are formed between isovalent and isomorphic con-

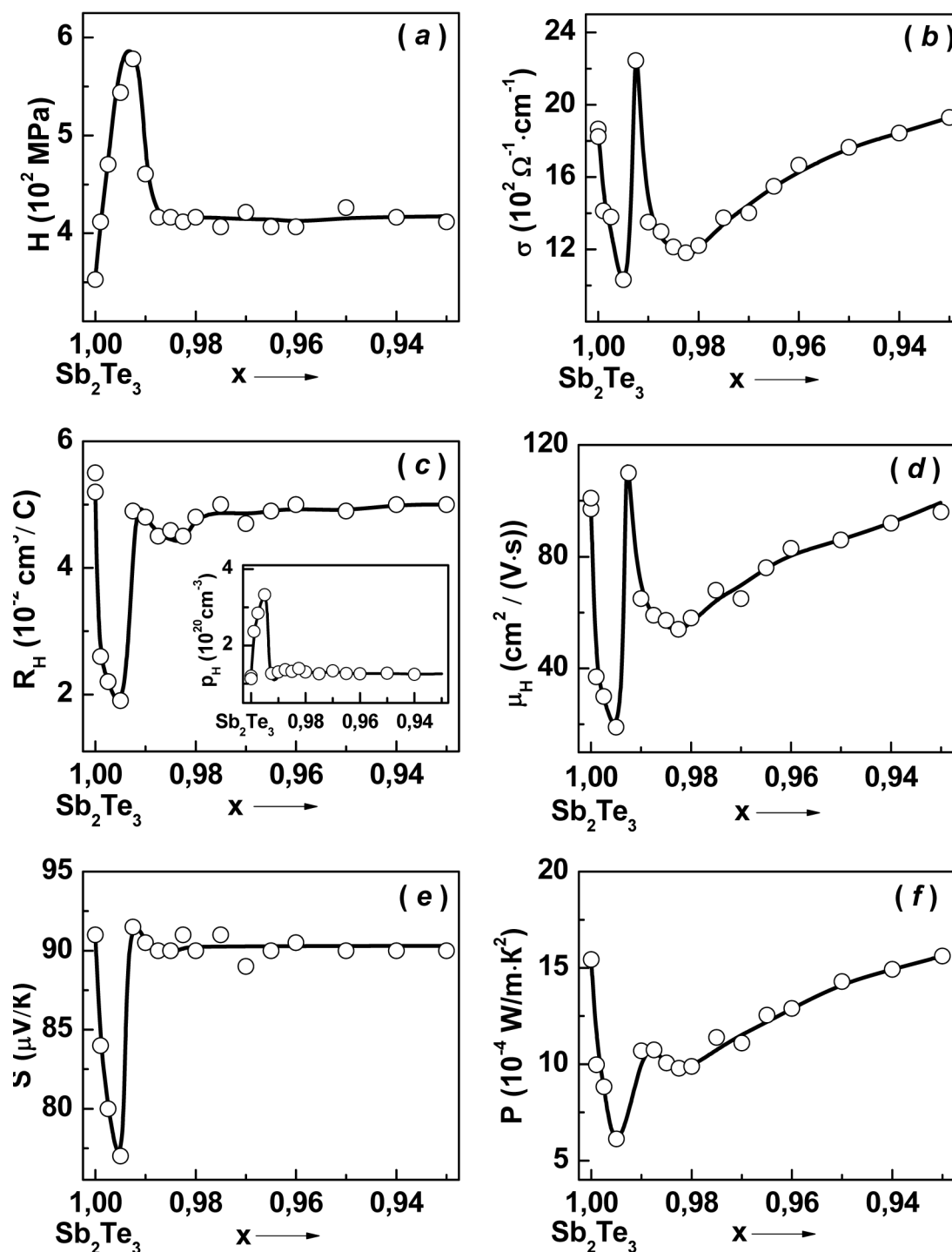Figure 1 Dependencies of microhardness H (a), electrical conductivity σ (b), the Hall coefficient R_H (c) (insert: the Hall charge carrier concentration p_H), the Hall charge carrier mobility μ_H (d), the Seebeck coefficient S (e), power factor $P = S^2 \sigma$ (f) on composition x of the $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions

gruently melting Bi_2Te_3 and Sb_2Te_3 compounds by cation $Sb \rightarrow Bi$ substitution. One might expect that the dependences of various properties on the composition are smooth curves, which is consistent with the data of a number of works [14–21]. However, as noted above, in these works, a small number of alloys of various compositions with a large step in concentration were studied. Therefore, the complex nature of the concentration dependences of the properties observed in the present work in the range $x = 1.0 - 0.93$ needs to be explained.

When implementing the $Sb \rightarrow Bi$ substitution scheme, Bi_2Te_3 introduced into the Sb_2Te_3 crystal lattice should be an electrically neutral additive that does not change the hole concentration. Meanwhile, it can be seen that the introduction of the first portions of Bi_2Te_3 leads to a sharp increase in p_H (~3.5 times), and, accordingly, to the sharp change in the galvanomagnetic (R_H, μ_H) and TE (S) coefficients (Fig. 1, b-e). To explain this fact, it should be taken into account that the Sb_2Te_3 and Bi_2Te_3 compounds of stoichiometric composition already contain p-type charge carriers and the corresponding defects of the crystal lattice, which are formed in accordance with the features of the Bi–Te and Sb–Te equilibrium phase diagrams [24].The main type of equilibrium defects that determine the p-type conductivity in Sb_2Te_3 and Bi_2Te_3 are Sb_{Te} and Bi_{Te} antisite defects [24-28].

The introduction of a Bi impurity into Sb_2Te_3 by cationic substitution can lead to a change in the conditions of thermodynamic equilibrium and cause a change in the equilibrium concentration of Sb_{Te} defects or lead to the formation of some another p-type defects. A sharp increase in p_H when the first "foreign" Bi atoms appear in the crystal lattice, accompanied by a decrease in R_H, σ, μ_H and S, means that in the indicated x range the conditions of thermodynamic equilibrium change and new defects of p-type appear. However, with a further increase in the concentration of Bi atoms, the number of these defects is greatly reduced, p_H decreases, R_H, σ, μ_H and S increase, and, starting from $x \sim 0.98$, the substitution scheme approaches the isovalent scheme, at which the concentration of charge carriers does not change.

Thus, in the studied concentration range ($x = 1.0 - 0.93$), three subregions can be distinguished: $x = 1.0 - 0.995$, $x = 0.995 - 0.98$, and $x = 0.98 - 0.93$. The first subregion corresponds to a dilute solid solution, when the number of IAs randomly distributed over the crystal is small and they do not interact with each other. An increase in the concentration of p-type charge carriers, even though the cationic substitution of $Sb \rightarrow Bi$ is isovalent, indicates a change in the conditions of thermodynamic equilibrium in Sb_2Te_3 upon the introduction of the first portions of IAs. In the second subregion, the presence of peaks in $H(x)$, $\sigma(x)$, $R_H(x)$, $S(x)$, $p_H(x)$ and $\mu_H(x)$ dependences indicates the presence of a concentration phase transition. In the third subregion, the properties change monotonically, and p_H does not change with composition, which is consistent with isovalent substitution.

A qualitative change in the nature of the dependence of properties on composition with a change in the concentration of IAs in the second subregion can be justified from a thermodynamic point of view by writing an expression for the change in free energy F in the simplest case without taking into account changes in external conditions (temperature, pressure, volume, etc.) and state of material (single or polycrystal, bulk sample or film, etc.):

$$\Delta F = \Delta U - T\Delta S, \qquad (1)$$

where ΔF, ΔU, and ΔS are the free energy, internal energy, and configurational entropy changes, accordingly, and T is the absolute temperature. At a low IAs concentration, when the interaction of IAs with each other can be neglected, an increase in the number of structural defects is stimulated by a sharp increase in the configurational entropy, which is not compensated by a simultaneous increase in the crystal internal energy. However, as the concentration of IAs increases, the situation changes and the further formation of new noninteracting defects will no longer be thermodynamically favorable, and this will lead to a change in the nature of the concentration dependences of properties.

One of the models that can predict the presence of a phase transition during the transition from dilute to concentrated solid solutions, the critical concentration value, and the nature of the concentration dependence of properties during such a transition is the percolation model [5,6]. Using the basic ideas of the percolation theory, we can talk about the formation at a certain concentration of Bi atoms ("percolation threshold") of an "infinite cluster" penetrating the entire crystal, that is, about the realization of a percolation phase transition. In this case, the properties of a crystal change qualitatively.

Until the percolation threshold is reached, the properties change as in a dilute solid solution. The elastic deformation fields generated by individual IAs practically do not overlap, and each IA makes an additive contribution to the value of H, and the dependence of H on the composition is close to linear [29-31]. The main reason for hardening is the elastic interaction of dislocations with dissolved IAs, which block the movement of dislocations, leading to a decrease in their mobility and, accordingly, to hardening.

A sharp increase in p_H value of the Sb_2Te_3 in the region $x = 1 - 0.995$ shows that the conditions of thermodynamic equilibrium change, which leads to an increase in the equilibrium concentration of antisite defects in Sb_2Te_3. With the introduction of IAs, the mobility of charge carriers μ_H decreases due to their scattering on IAs, and as a result, the values of σ decrease.

A sharp drop in H in the second subregion indicates a change in the character of dislocation movement, the increase in their mobility and cannot be explained within the framework of theories of solid solution strengthening. In a number of our works, the effect of H decreasing, σ and μ_H increasing in the region of low impurity content was observed and explained within the framework of the percolation theory [11-13]. These phenomena were attributed to the collective interaction of the deformation fields of IAs, when their concentration reaches the percolation threshold x_c, corresponding to the formation of an "infinite cluster".

Reaching the percolation threshold stimulates self-organization processes in the subsystem of defects (short-range or long-range ordering), which, in the presence of certain conditions, can lead to the formation of ordered structures. The probability of the Coulomb interaction between the introduced oppositely charged Sb^{+3} and Te^{+2} ions increases, which stimulates the process of chemical interaction with the formation of electrically neutral Bi_2Te_3 complexes. When such complexes form, Bi_2Te_3, rather than individual Bi and Te atoms, can be considered as a substitution component. In this case the Sb_2Te_3 - Bi_2Te_3 section of the Sb-Bi-Te ternary system can be considered as a quasi-binary section, which is not true in the case of a dilute solid solution. Based on this, one can conclude that in the case of a solid solution between two stable compounds, in the region of low concentrations of the introduced component, the solid solutions are, strictly speaking, not quasi-binary. Taking it into account and using the concepts of percolation theory, we can say that the percolation threshold can be considered as a conditional boundary in the transition to "true quasi-binary behavior".

5. Conclusions

1.   The dependences of mechanical, galvanomagnetic and thermoelectric properties on composition of the polycrystalline $(Bi_{1-x}Sb_x)_2Te_3$ solid solutions in the range of $x = 1 - 0.93$ were obtained at room temperature.

2.   In the composition dependences of microhardness, electrical conductivity, the Hall and Seebeck coefficients, charge carrier mobility, and thermoelectric power factor, the anomalies are observed in the range $x = 0.995 - 0.98$, which indicates the presence of a phase transition. It is assumed that this phase transition has a percolation nature.

3.   The obtained results are another confirmation of our earlier stated idea that the existence of the critical phenomena accompanying a percolation type phase transition in the range

of small concentration of the introduced component is characteristic of all solid solutions.

4.   It is suggested that in the case of sections of a ternary system passing through two stable chemical compounds in the Gibbs concentration triangle, the percolation threshold can approximately correspond to the compositions at which the "true quasi-binary behavior" of the alloys starts.

5.   The concentration-dependent anomalies of properties associated with the presence of a percolation-type transition should be taken into account when developing new materials and optimizing the properties of materials by doping.

References

1. D.M.Rowe, Thermoelectric Handbook, Macro to Nano. CRC Press, Taylor & Francis Group, Boca Raton (2006).
2. C.Uher, Materials Aspect of Thermoelectricity. CRC Press, Boca Raton (2016).
3. H.J.Goldsmid, Introduction to Thermoelectricity. Springer-Verlag, Berlin, Heidelberg, Germany (2016).
4. V.M.Glazov, L.M.Pavlova, Chemical thermodynamics and phase equilibria. Metallurgy, Moscow (1988) [in Russian].
5. D.Stauffer, A.Aharony, Introduction to Percolation Theory. Taylor & Francis, London/Washington, DC (1992).
6. B.I.Shklovskii, A.L.Efros, Electronic Properties of Doped Semiconductors. Springer, Berlin, Heidelberg (1984).
7. E.I.Rogacheva, I.M.Krivulkin, V.P.Popov et.al., *Phys. Stat. Sol.(a)*, **148**, K65 (1995).
8. E.I.Rogacheva, A.A.Drozdova, O.N.Nashchekina, *Phys. Stat. Sol. (a)*, **207**, 344 (2010).
9. E.I.Rogacheva, A.N.Doroshenko, O.N.Nashchekina et.al., *Appl. Phys. Letters*, **109**, 131906 (2016).
10. E.I.Rogacheva, A.N.Doroshenko, T.I.Khramova et.al., *J. Phys. Chem. Solids*, **143**, 109431 (2020).
11. E.I.Rogacheva, *Jpn. J. Appl. Phys*, **32**, 775 (1993).
12. E.I.Rogacheva, *J. Thermoelectricity*, **2**, 61 (2007).
13. E.I.Rogacheva, O.N.Nashchekina, in: Advanced Thermoelectric Materials. John Willey & Sons, Scrivener Publishing LLC (2019), p. 383.
14. H.Scherrer, in: Handbook of thermoelectric. CRC Press, London, New York, Washington, Boca Raton, D.C. (1995), p.213.

15. M.J.Smith, R.J.Knight, C.W.Spencer, *J. Appl. Phys.*, **33**, 2186 (1962).

16. L.R.Testardi, J.N.Bierly, F.J.Donahoe, *J Phys Chem Solids*, **23**, 1209 (1962)

17. C.H.Champness, P.T.Chiang, P.Parekh, *Canad. J. Physics*, **43**, 653 (1965).

18. H.-W.Jeon, H.-Ph.Ha, D.-B.Hyun et.al., *J. Phys. Chem. solids*, **52**, 579 (1991).

19. L.D.Ivanova, Yu.V.Granatkina, *Inorg. Mater.* **36**, 672 (2000).

20. L.D.Ivanova, L.I.Petrova, *Inorg. Mater*., **43**, 933 (2007).

21. K.Martynova, E.Rogacheva, *Funct. Mater.*, **25**, 54 (2018).

22. E.I.Rogacheva, K.V.Martynova, A.S.Bondarenko, *J. Thermoelectricity*, **5**, 47 (2016).

23. S.I.Bulychev, V.P.Alyokhin, Testing of materials by continuous indentation of the indenter. Mashinostroenie, Moscow (1990) [in Russian].

24. T.Caillat, M.Carle, D.Perrin et.al., *J. Phys. Chem. Solids*, **53**, 227 (1992).

25. G.R.Miller, C.-Y.Li, *J. Phys. Chem. Solids*, **26**, 173 (1965).

26. G.Ghosh, H.L.Lukas, L.Delaey, *Z. Metallkde*, **80**, 731 (1989).

27. E.I.Rogacheva, A.V.Budnik, O.S.Vodorez et.al., *J. Thermoelectricity*, **6**, 42 (2014).

28. T.Zhu, L.Hu, X.Zhao, *Adv. Sci*, **3**, 1600004 (2016).

29. T.Suzuki, H.Yoshinaga, S.Takeuchi, Dislocation Dynamics and Plasticity. Mir, Moscow (1989) [in Russian].

30. R.L.Fleischer, *Acta Met.*, **11**, 203 (1963).

31. R.Labusch, *J. Appl. Phys.*, **39** (9), 4144 (1968).