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**PECULIARITIES OF THE CONCENTRATION
DEPENDENCES OF STRUCTURAL
AND THERMOELECTRIC PROPERTIES
IN SOLID SOLUTIONS *PbTe-PbSe***

*New experimental results and an overview of the results obtained earlier by the authors on the dependences of structure, mechanical, galvanomagnetic and thermoelectric properties on the composition of isovalent semiconductor solid solutions *PbTe-PbSe* in the range of small concentrations of *PbSe* (0 – 5 mol.%) as well as on the temperature dependences of galvanomagnetic properties (80 – 300 K) are presented. For the first time within the studied range of concentrations, an anomalous increase in electrical conductivity, charge carrier mobility and the exponent in the temperature dependence of charge carrier mobility under increasing *PbSe* content and an oscillatory behavior of the dependences of X-ray linewidth, microhardness, the Hall coefficient and the Seebeck coefficient on composition were registered. The observed effects are attributed to the existence of a percolation-type phase transition, presumably typical for all solid solutions, and to the self-organization processes occurring in solid solutions under the transition to the impurity continuum.*

Key words: *PbTe-PbSe* solid solution, composition, heat treatment, percolation threshold, temperature dependence, microhardness, diffraction line width, electroconductivity, charge carrier mobility, Hall coefficient, Seebeck coefficient.

Introduction

The solid solution method proposed far back by academician A.F. Ioffe is still one of the main methods for improving the thermoelectric (TE) figure of merit Z of materials ($Z = S^2\sigma/\lambda$, where S is the Seebeck coefficient, σ is electric conductivity, λ is thermal conductivity) [1-3]. In so doing, it is generally supposed that increase in the concentration of introduced component is accompanied by a monotonous change in TE properties. However, in a number of solid solutions based on semiconductor compounds of the type IV-VI (*PbTe*, *SnTe*, *GeTe*) we have discovered a nonmonotonous character of concentration dependences of various properties in the region of low impurity content (see, for instance, [4-9]) and it was conjectured [10, 11] that the observed effect is typical of all solid solutions and is due to critical phenomena attending a transition from the dilute to concentrated solid solutions.

Recently, when investigating the concentration dependences of TE properties of *PbTe*-based solid solutions in *PbTe-Bi₂Te₃* system we have discovered [12] another effect, namely an oscillatory behaviour of the composition dependences of properties, which we attributed to structural rearrangements occurring in a concentrated solid solution with increase in impurity content.

The importance of observed effects in terms of TE material science stimulates the expansion of the scope of investigated solid solutions and a more detailed study of the concentration dependences of properties. In particular, it is interesting to clear out whether the above effects will manifest

themselves on composition-property dependences in case of isovalent and isostructural solid solutions. Such materials include solid solutions *PbTe-PbSe*, promising TE materials used in thermogenerators working in medium-temperature region (600 – 900 K) [2, 3]. Note that exactly this system was one of the first to demonstrate the efficiency of using the solid solution method for *Z* increase.

Binary compounds *PbTe* and *PbSe* are crystallized in the structure of *NaCl* type with the unit cell parameters $a = 0.645$ nm and $a = 0.612$ nm, respectively [13]. These are nonstoichiometric compounds with double-sided homogeneity areas with *n*-type conductivity at lead excess and *p*-type conductivity at chalcogen excess. The maxima on the liquidus and solidus curves in *Pb-Te* and *Pb-Se* systems do not coincide with the stoichiometric composition, being slightly displaced toward *Te* excess (50.002 at.%) or *Se* excess (50.005 at.%), which determines *p*-type conductivity of stoichiometric compositions *PbTe* and *PbSe* and undoped solid solutions *PbTe-PbSe* [13]. *PbTe* and *PbSe* have a complicated structure of valence band consisting of two overlapping subbands with different density of states [14].

PbTe and *PbSe* form a continuous series of isovalent and isostructural solid solutions with a minimum at 18 mol.% *PbSe* [13]. Depending on composition, the unit cell parameter changes in a linear fashion, with a slight negative deviation from linearity [13, 15], and microhardness grows as compared to the initial compounds, forming a curve with a maximum [16]. As far as we know, neither of the works dealing with the unit cell parameter and microhardness have studied alloys with *PbSe* content less than 5 mol.%. The energy gap of *PbTe-PbSe* alloys determined by self-absorption edge is a monotonous function of composition and almost linearly increases with increasing *PbSe* content [14, 15]. In [17], TE properties of solid solutions *PbTe-PbSe* of both *n*- and *p*-type were studied. Research on *Na*-doped *p-PbTe-PbSe* (0 – 15 mol.% *PbSe*) alloys has shown that the use of solid solutions allows reducing phonon thermal conductivity without major deterioration of electrical properties and that maximum value of *Z* ($Z = 2.0 \cdot 10^{-3} \text{ K}^{-1}$) exceeding by 30 % the value of *Z* for *p-PbTe* is achieved at 650 K for a solid solution with 5 mol.% *PbSe* and 0.7 at.% *Na*.

The existing works on TE properties of solid solutions *PbTe-PbSe* are mainly concerned with doped alloys of electron or hole types with different impurity concentration. In these works, the compositions and doping level optimal from the standpoint of practical applications, that is, with maximum *Z* values, are determined. However, to reveal the concentration anomalies of properties related to transition into heavy doping area, investigations should be conducted on the undoped stoichiometric solid solutions, where the role of impurity is played by the second component (in the case at hand it is selenium).

In [18-22] we reported on the results of measuring various properties of solid solutions *PbTe-PbSe* in the range of concentrations not exceeding 5 mol.% *PbSe*. It was established that isotherms of microhardness *H*, the Seebeck coefficient *S*, the Hall coefficient R_H , electric conductivity σ and the Hall mobility of charge carriers μ_H comprise anomalous parts on which a monotonous change of properties with composition is violated.

The purpose of this work is a more detailed additional study and analysis of the character of change in the structure and TE properties depending on the composition and temperature in the undoped polycrystalline solid solutions *PbTe-PbSe* in the range of compositions 0 – 5 mol.% *PbSe*. As long as in the manufacture of TE devices wide use is made of material pressing which allows increasing the strength and homogeneity degree of samples as compared to cast ones and generally followed by annealing, a question arises as to the relation between the characteristics of cast and pressed, annealed and unannealed samples of the same material.

Having analyzed the obtained results, we managed to reveal new effects taking place in solid solutions under study and governing the specific character of the composition and temperature dependences of TE properties.

Experimental procedure

Polycrystalline samples of $PbTe$ - $PbSe$ system (0 – 5 mol.% $PbSe$) were prepared by direct alloying of Pb , Te and Se elements of high degree of purity (99.999 % of basic component) in evacuated quartz ampoules at a temperature of 1250 ± 10 K for 6 hours with the use of vibratory agitation and subsequent annealing at a temperature of ~ 870 K for 250 hours (series 1). Some of the samples of series 1 were used to manufacture pressed samples at a temperature of 670 K and pressure 400 MPa (series 2), which after measurement were subject to homogenizing annealing in vacuum at 770 K for 260 hours (series 3). Besides, in the range of concentrations 0 – 2.5 mol.% $PbSe$ the alloys were subject to additional heat treatment, namely after the synthesis the alloys were annealed at a higher temperature 1020 K for 200 hours (series 4). The alloys of each series were prepared simultaneously, so as to assure the identical conditions of their production. X-ray spectroscopy and chemical analysis methods were used to establish the homogeneity of samples. It was shown that a deviation of chemical composition from the assigned value did not exceed ± 0.02 at.%.

Microhardness was measured at room temperature on PMT-3 microhardness tester, using a diamond pyramid, under a constant load on the indenter $P = 0.49$ N. To establish the necessary load value, prior to measurement of H , dependences $H(P)$ were studied in the range of $P = 0.03 - 0.49$ N, and it was shown that H is reduced with increase in P and is practically independent of load, starting from $P \sim 0.30$ N. As an example, Fig. 1 shows dependences $H(P)$ for alloys of series 4. The time of loading, the time of exposure to load and the time of unloading were 10 s each. Device adjustment was performed using fresh chips of $NaCl$ crystals. Surface preparation for measuring H (grinding, mechanical polishing and etching) was identical for all samples. Measuring H of each sample was performed at least at 30 points of a sample with subsequent statistical processing of results. Relative mean-square fluctuation for all samples did not exceed 3 %.

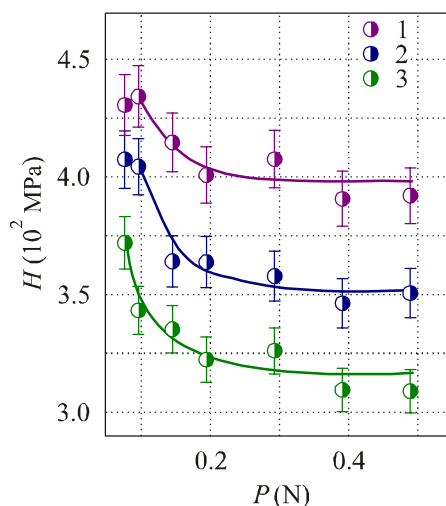


Fig. 1. Microhardness of solid solutions $PbTe$ - $PbSe$ versus the load on the indenter: 1 – $PbTe$, 2 – 1 mol.% $PbSe$, 3 – 1.5 mol.% $PbSe$.

The unit cell parameters a were determined on X-ray diffractometer DRON-2 with the Bragg-Brentano focusing geometry in filtered radiation of X-ray tube copper anode to an accuracy not lower than $\Delta a = 2 \cdot 10^{-4}$ nm.

The Hall coefficient R_H and electric conductivity σ were measured with the use of standard dc method in the range of temperatures from 80 to 300 K. The error of measuring R_H and σ did not exceed 5 %. The Hall mobility was calculated by the formula $\mu_H = \sigma \cdot R_H$. The Seebeck coefficient S was measured

by compensation method according to copper electrodes at room temperature at no fewer than 20 sample points with subsequent statistical processing of measured data. The root mean square relative error for all samples did not exceed 3 %. All the samples, except for samples of series 3, were of *p*-type conductivity.

Discussion of the results

According to the results of microstructural and X-ray diffraction analyses, over the entire investigated range of compositions the alloys were single-phase and had crystalline structure of *NaCl* type. Fig. 2, a shows a dependence of the unit cell parameter on the composition of *PbTe-PbSe* alloys in the range of 0 – 5 mol.% *PbSe* for series 1 and 4 at room temperature. It is seen that for both series the points fall on one straight line which to a high accuracy corresponds to the Vegard line, confirming the fact of formation of a continuous series of solid solutions in the investigated range of concentrations.

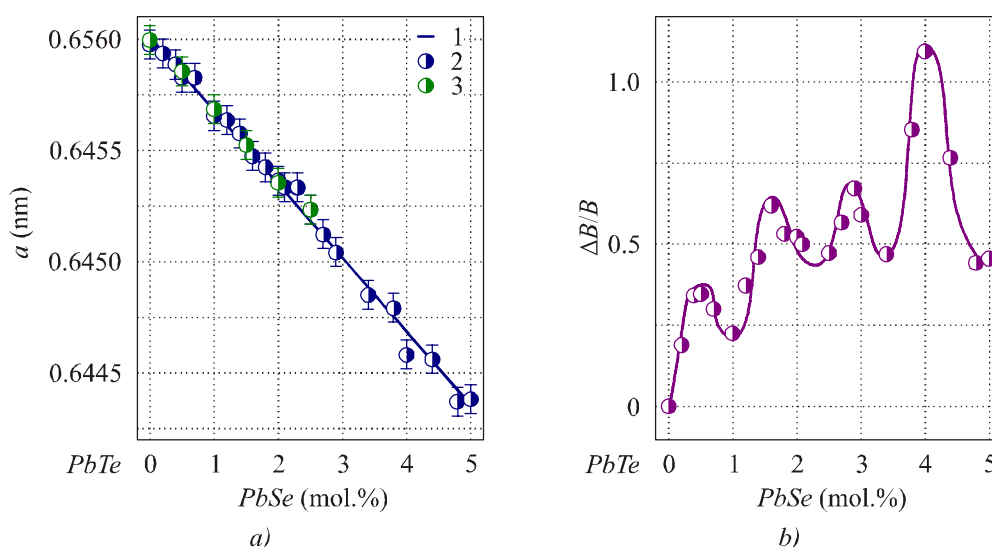


Fig. 2. Dependence of unit cell parameter *a* (a) and a relative change in diffraction line width $(644)_a + (820)_a$ $\Delta B/B$ (b) on the composition of solid solution *PbTe-PbSe* for samples of series 1.
 a) 1 – the Vegard curve; 2 – series 1; 3 – series 4.

Unlike the unit cell parameter, dependence of X-ray line width *B* on the composition of alloys is not monotonous. From Fig. 2, b it is evident that with a general tendency to growth of relative change in $\Delta B/B$ with increasing *PbSe* concentration, the dependence has a distinct oscillatory behaviour.

Fig. 3 shows dependences of *H* on the composition of *PbTe-PbSe* alloys prepared with the use of various techniques, and it is seen that neither of these dependences is monotonous, which was to be expected at formation of a perfect solid solution. On introduction of the first portions of *PbSe* (up to ~ 0.5 mol.%), the value of *H* for all series of samples is increased, pointing to crystal strengthening with introduction of Se impurity. However, with further increase in *PbSe* concentration, the behaviour of *H* – composition dependences is different for different series, though the general tendency to *H* increase within the entire concentration range (0 – 5 mol.% *PbSe*) is retained. Thus, for cast samples of series 1 in the range of compositions 0.5 – 1.25 mol.% *PbSe* there is a horizontal pad on the dependence; a similar pad is also observed for pressed unannealed samples (series 2), but its concentration range is somewhat expanded (0.5 – 1.75 mol.% *PbSe*). In so doing, for pressed samples there is a more considerable *H* increase in the range of 0 – 0.5 mol.% *PbSe* than for cast samples, though *H* values of series 1 and 2, achieved on the boundary of investigated composition range, are practically identical. Annealing of pressed samples in vacuum (series 3) leading to inversion of conductivity sign (*p* → *n*) changes

considerably the composition dependence of H : in the range of 0.5 – 2.5 mol.% $PbSe$ on the isotherm of H there are distinct oscillations, following which H increases drastically when approaching the composition of 5 mol.% $PbSe$ (Fig. 3, c). A similar oscillatory behaviour of H dependence is observed for cast samples subject to high-temperature annealing (series 4), that were prepared in the range of concentrations 0 – 2.5 mol.% $PbSe$. From Fig. 3, d it is seen that such oscillatory behaviour of the composition dependence of H is also retained for series 4 with a change in the indenter load.

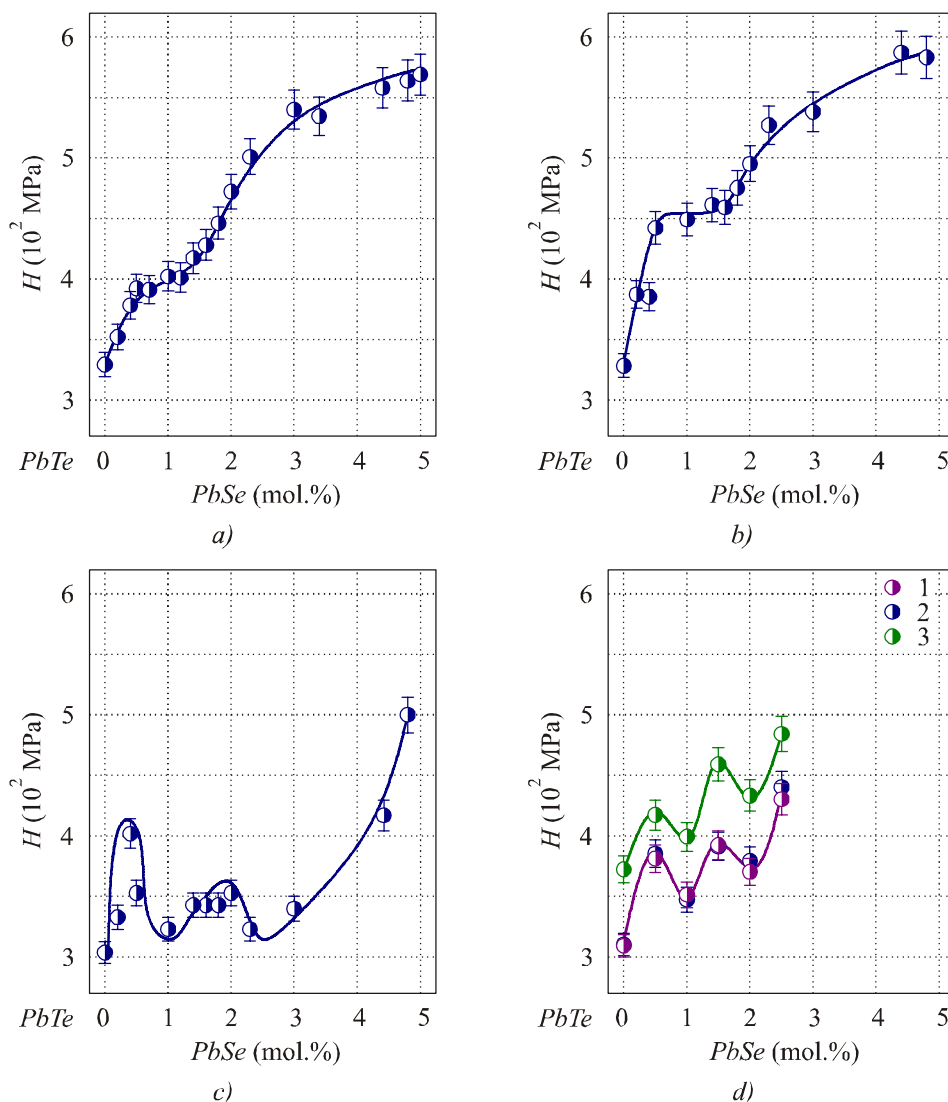


Fig. 3. Dependence of microhardness H on the composition of solid solution $PbTe-PbSe$ for samples prepared by different methods: a) – series 1; b) – series 2; c) – series 3 and d) – series 4: 1 – 0.049 N, 2 – 0.39 N, 3 – 0.49 N.

Thus, irrespective of sample preparation technique (cast or preseed) and heat treatment, introduction of up to 0.5 mol.% $PbSe$ leads to a drastic increase of H . The effect of solid-solution hardening on the introduction of impurities related to blocking of dislocations by impurity atoms is well known [23]. However, demands explanation the fact that starting from ~ 0.5 mol.% $PbSe$, for all series there is a qualitative change in dependence, namely the appearance of plateaus or oscillations.

Studies on the kinetic properties at room temperature have proved the existence of concentration anomalies in solid solutions $PbTe-PbSe$. From Fig. 4, a and b, showing dependences of σ and μ_H on

composition for cast polycrystalline samples of series 1, one can see that these dependences have a behaviour uncommon for solid solutions: after a drop in said parameters with increase in *PbSe* concentration to 0.5 – 0.75 mol.% there is a drastic (more than 100 %) growth of σ and μ_H over a sufficiently narrow concentration range, following which σ and μ_H again drop with increase in *PbSe* content to 5.0 mol.%. The parts of σ and μ_H drop with a growth in *PbSe* concentration can be adequately explained, since with introduction to crystal of impurity atoms the mobility of charge carriers is generally reduced due to increased imperfection of crystal lattice and the emergence of additional centres of charge carrier scattering, but growth of σ and μ_H from this standpoint is anomalous.

Even more complicated composition dependence is observed for the Hall and Seebeck coefficients (Fig. 4, *c, d*): up to ~ 2.5 mol.% *PbSe*, despite the general tendency to reduction of R_H and S with a growth in concentration *PbSe*, parts of drop in R_H and S interchange with parts of growth, owing to which the composition dependence of R_H and S exhibits a distinct oscillatory behaviour.

The nonmonotonous behaviour of kinetic coefficients is also responsible for a complicated dependence of TE power $P = S^2 \sigma$ on the composition (Fig. 4, *e*).

Research on the effect of pressing on the values of S , σ and μ_H of polycrystals of solid solutions *PbTe-PbSe* in the range of concentrations 0 – 5.0 mol.% *PbSe* at room temperature performed in [21] has shown that in pressed samples the values of S remain almost unchanged, and σ and μ_H are reduced as compared to cast samples. Annealing of pressed samples leads to a reversal of hole to electron conductivity type, growth of σ and μ_H . However, concentration anomalies of properties in the range of compositions 0.5 – 2.5 mol.% *PbSe*, observed in cast samples and presumably related to a transition to impurity continuum also occur in pressed samples, confirming the fact of existence of percolation-type concentration phase transition.

Fig. 5 shows the temperature dependences of σ , μ_H and R_H for samples of series 1 of various composition. All the samples have *p*- conductivity over the entire investigated range of temperatures and compositions. For samples of all compositions a rise in temperature leads to a monotonous decrease in σ and μ_H and a slight increase in R_H . Unlike other lead chalcogenides, where, as a rule, $R_H(T)$ dependence in the range from helium to room temperature and higher is very weak, in *p-PbTe* at higher than 150 K there is a marked growth of R_H . Such R_H behaviour in *p-PbTe* is attributable to the influence of the second valence band characterized by larger effective mass and located below the edge of light holes at the distance of order 0.1 eV. Due to a low mobility and a larger effective mass of holes in the second valence band, their contribution to the Hall effect is relatively small, and as the holes go over to the second band, with a rise in temperature, the effective concentration of charge carriers is decreased, and R_H is increased. Taking into consideration the presence of light and heavy holes, the expression for R_H can be written as follows:

$$R_H = \frac{r}{e} \frac{p_1 \mu_1 + p_2 \mu_2}{(p_1 \mu_1 + p_2 \mu_2)^2} = \frac{r}{ep_1} \frac{1 + \gamma f^2}{(1 + \gamma f)^2}, \quad (1)$$

where p_1 and p_2 are concentrations of light and heavy holes, respectively, the sum of which does not depend on temperature and is equal to the number of acceptors, μ_1 and μ_2 are their mobilities, $\gamma = p_1 / p_2$, $f = \mu_1 / \mu_2$, r is Hall-factor depending on the degeneracy degree and the mechanism of charge carrier scattering. From formula (1) it follows that as the contribution of heavy holes increases with a rise in temperature, R_H increases as well. As is evident from Fig. 5, *a, b, c*, a similar effect occurs in solid solutions *PbTe-PbSe*, whose valence band structure is identical to that of lead telluride.

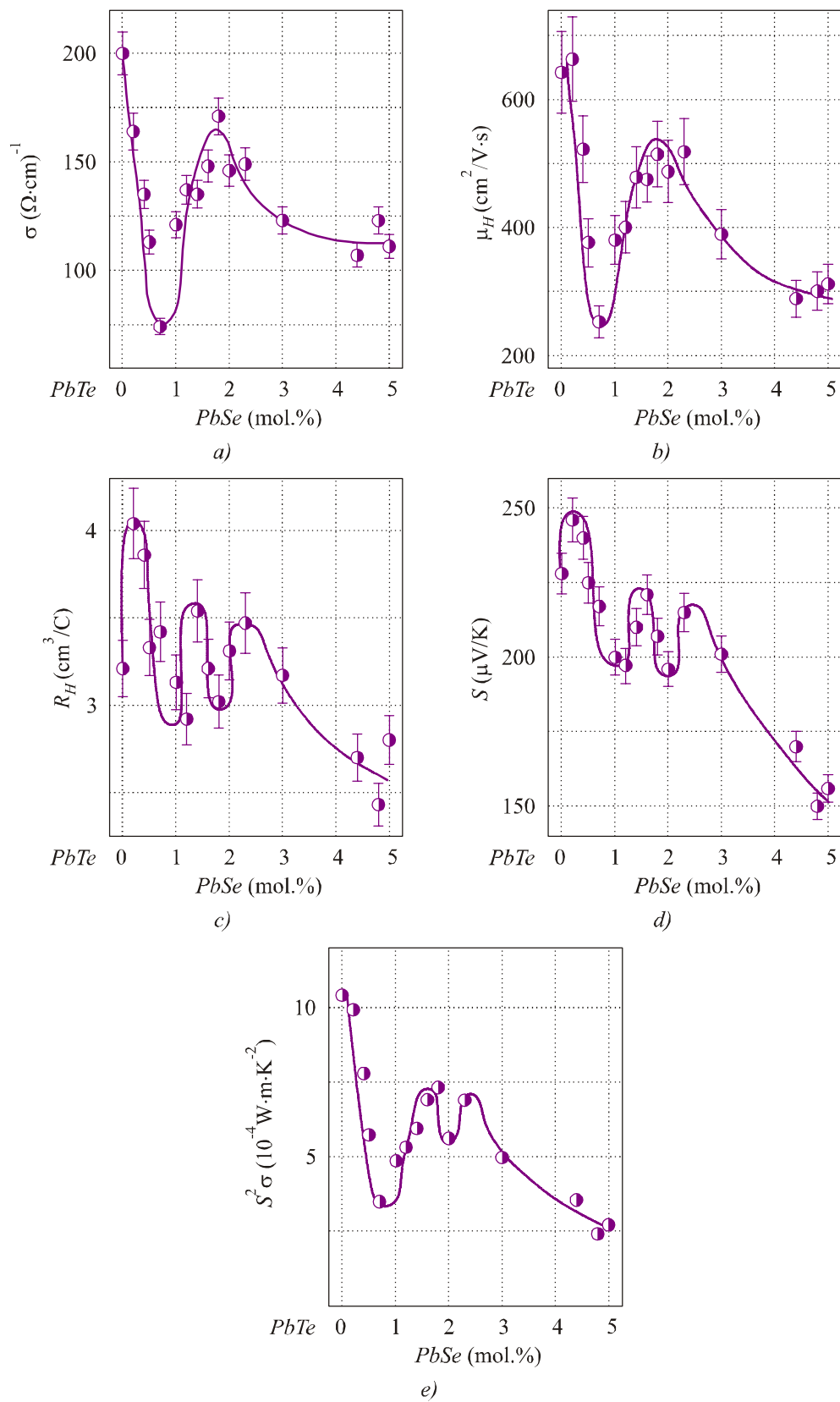
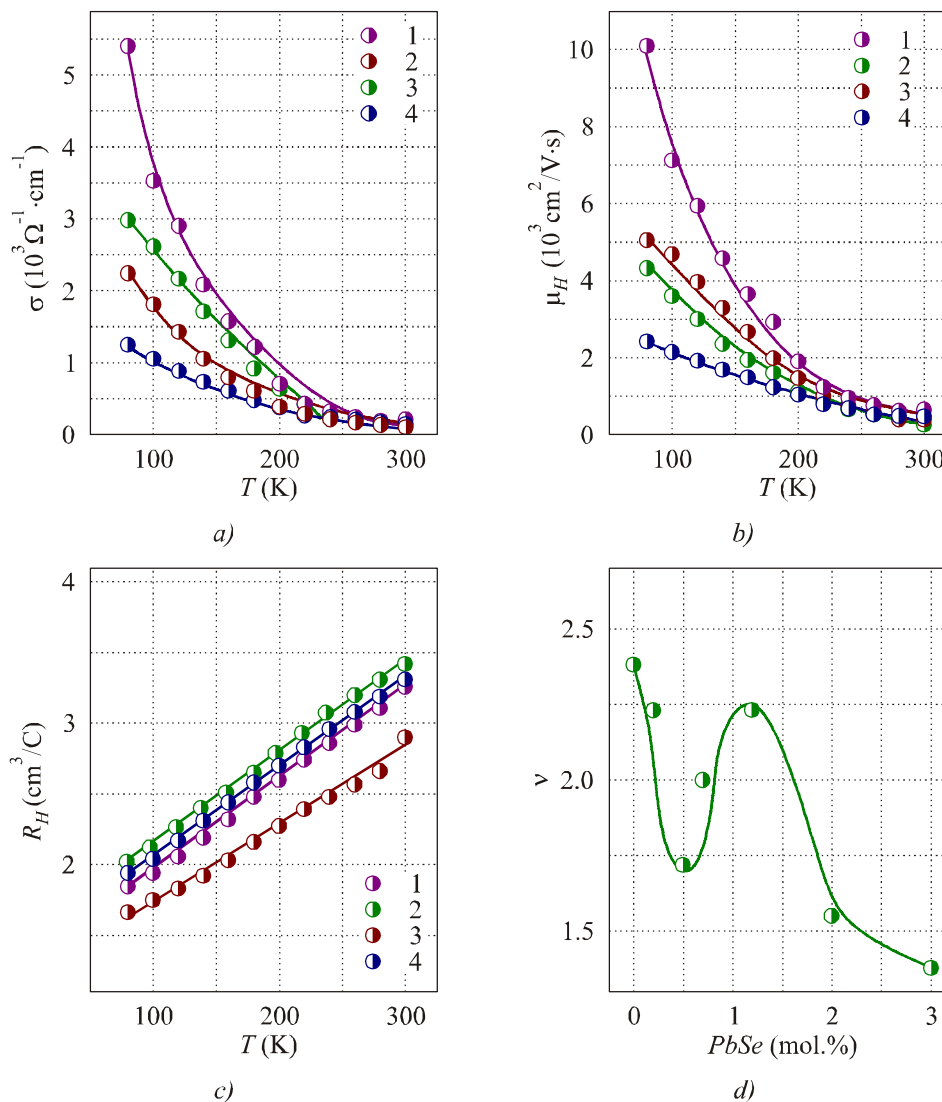


Fig. 4. Dependence of electric conductivity σ (a), Hall mobility of charge carriers μ_H (b), Hall coefficient R_H (c), Seebeck coefficient S (d) and thermoelectric power $P = S^2\sigma$ (e) on the composition of solid solutions PbTe-PbSe for samples of series 1.

Of interest is the composition dependence of exponent ν in the temperature dependence of charge carriers mobility $\mu_H \sim T^\nu$ (Fig. 5, d), which, as the other characteristics, has a nonmonotonous behaviour. With a general tendency to drop of ν with increasing *PbSe* content, the curve has an anomalous part of exponent growth, which is additional proof of a complicated concentration dependence of properties in a solid solution *PbTe-PbSe*.



*Fig. 5. Temperature dependences of electric conductivity σ (a), Hall mobility of charge carriers μ_H (b), Hall coefficient R_H (c) and exponent ν in the temperature dependence $\mu_H = A \cdot T^\nu$ (d) 1 – *PbTe*; 2 – 0.7 mol.% *PbSe*; 3 – 1.2 mol.% *PbSe*; 4 – 2.0 mol. % *PbSe*.*

For a qualitative explanation of a change in the composition dependence of properties, observed for all properties, starting from ~ 0.5 mol.% *PbSe*, one can use the concepts of percolation theory, as we did it for other semiconductor solid solutions [4-11]. It is supposed that in any solid solution, irrespective of the character of impurity interaction, there exists a critical concentration x_C – “percolation threshold”, whereby a continuous chain of interactions between impurity atoms is formed (“infinite cluster” in terms of percolation theory) [24]. As long as percolation transition refers to second-order phase transitions, it must be attended with critical phenomena, that is, a drastic change in properties. Using percolation theory approximation, it can be assumed that the onset of anomalous portions corresponds to reaching percolation threshold x_C , and in the concentration ranges corresponding to anomalous change of

properties the density of infinite cluster is increased. On completion of the latter process, crystal goes over into a new state, i.e. impurity continuum, when impurity atoms become interconnected and their interaction acquires a cooperative nature. We think that exactly percolation threshold might serve the boundary that separates dilute solid solutions from concentrated ones. Of course, in the general case for various properties defined by various interaction types (deformation, Coulomb, dipole-dipole, etc), the values of percolation thresholds x_C for the same system can be different. However, in *PbTe-PbSe* system under investigation these values almost coincide – the anomalies start from $\sim 0.5 - 0.75$ mol.% *PbSe*.

Let us consider as an example such property as microhardness. It is known that the basic mechanism of solid-state hardening is related to elastic interaction of dislocation fields and impurity atoms, as a result of which the dislocation mobility is reduced, hence, strength characteristics, such as yield strength, microhardness, etc., increase. As long as marked displacements of atoms are created at the distance of one or two atomic spacings, one can consider the field of elastic deformations to be short-range and speak of a typical radius of deformation interaction r_0 . With low impurity concentrations (in this case *Se* atoms), when the distance between them is much larger than r_0 , the fields of elastic deformations created by individual impurity atoms are isolated from each other, almost not overlapped and make an additive contribution to H value. This results in H growth with increasing impurity concentration, which is observed in the range to ~ 0.5 mol.% *PbSe*.

With further increase in impurity atoms content for samples of series 1 and 2 on the isotherm of H there appear plateau in the range of $0.5 - 1.25$ and $0.5 - 1.75$ mol.% *PbSe*, respectively, and for samples of series 3 and 4 this dependence acquires oscillatory behaviour in the range of compositions $0 - 2.5$ mol.% *PbSe*. This fact testifies to the presence of concentration phase transition which in the general case can be due to solid solution decomposition or rearrangement of crystal or electronic structure. The assumption of possible decomposition or change in crystal structure contradicts the results of X -ray structural analysis. The presence of anomalies on the curve $H -$ composition points to a change in dislocation motion pattern, owing to which the dislocation motion grows and crystal softening occurs. This can be explained as follows. With increasing impurity concentration, the fields of elastic deformations start to be overlapped, leading to partial stress relief in a crystal. As long as impurity atoms are distributed in crystal lattice nonuniformly, some deformation spheres are overlapped, and the others – not, and portions with reduced stresses are formed in a crystal, which up to a certain concentration of impurity atoms are not interrelated. However, when concentration of impurity atoms becomes such that a continuous chain is formed, penetrating the entire crystal and interrelating impurity atoms through their deformation fields, the character of concentration dependence H should change, since dislocation motion pattern will change under the effect of applied load. As long as overlapping of deformation fields of two neighbouring atoms results in partial compensation of elastic stresses of opposite sign, formation of percolation channels will be matched by a drastic increase in dislocation mobility, hence, a decrease in H . The specific mechanism of collective effect of impurities on crystal plastic properties, which is a function of many factors and governs crystal softening, is not known so far and calls for special consideration. After crystal goes over into a qualitatively new state, related to formation of “impurity condensate”, new centres appear which impede the dislocation motion, and H grows again.

As can be seen from Fig. 3, the character of H dependence on composition and the character of concentration anomaly in this area is affected by sample fabrication technique (cast or pressed), the presence or absence of annealing, as well as annealing temperature. It is quite natural to be expected, since the degree of phase transition smearing, the character of properties change with phase transition are essentially dependent on the defective structure of crystal, its homogeneity, kinetic factors which,

in turn, are largely determined by thermal treatment. It can be supposed that with a rise in annealing temperature of cast samples from 870 to 1020 K and with annealing of pressed samples, firstly, higher homogenization degrees are achieved than for samples of series 1 and 2, and, secondly, the number of interstitial atoms is increased, which for series 4, possibly, become predominant point defects, taking into consideration that annealing of pressed samples is followed by inversion of conductivity type, caused, apparently, by slight losses of chalcogen at annealing. Microscopic mechanisms leading to oscillatory behaviour of H with composition in the intermediate range of compositions corresponding to transition from dilute to concentrated solid solutions are as yet unknown, but it is clear that considerable role in the manifestation of concentration anomalies is played by self-organization processes (when H drops), alternating with defect accumulation processes (when H increases). This assumption is supported by the presence of oscillatory concentration dependence of X -ray linewidth $(644)_a + (820)_a$ (Fig. 2, b). It is known that the main factors causing X -ray lines widening include fluctuations of atomic spacings due to microstresses and small size of coherent scattering areas [25]. In homogeneous solid solutions widening can be caused by disorder in the distribution of atoms of different sort and statistical displacements of atoms surrounding impurity atom relative to their position in a perfect crystal. So, widening of lines on introducing the first portions of impurity atoms can be readily explained. As long as all the samples were prepared by the same procedure, and X -ray study was identical, the change in $\Delta B/B$ with a variation of impurity atoms concentration can be due to internal structural changes caused by disorder in the distribution of impurity atoms and the microstresses they caused. When impurity concentration reaches x_c , the lattice stresses are partially relieved and dependence behaviour is changed.

The observed anomalous growth of σ and μ_H also testifies to qualitative changes of solid solution properties with a variation of impurity content. We observed similar concentration anomalies of σ and μ_H in the investigation of other solid solutions (*PbTe-MnTe* [7], *PbTe-GeTe* [9] etc.) and also attributed them to critical phenomena attending concentration phase transitions.

Considering these critical phenomena within the percolation theory [24], one can estimate the radius of impurity atom domain r_o , using equation for problem of spheres:

$$\frac{4\pi}{3} \cdot N_c (2r_o)^3 \approx 2.7, \quad (2)$$

where N_c is the average number of sphere centres in unit volume corresponding to percolation threshold. Such estimate for solid solutions *PbTe-PbSe* yields the value $r_o \approx 1.5 a_0$ (a_0 is parameter of unit cell *PbTe*), which is in good agreement with the short-range character of impurity potential in compounds IV-VI [14].

Oscillatory behaviour of dependences of R_H , S , H and $\Delta B/B$ on composition with *PbSe* content less than $\sim 2.5 - 3.0$ mol.% shows that the system passes through a number of intermediate states with very close compositions, but different character of space correlations. Such behaviour can testify that, under certain concentrations of impurity components, self-organization processes interchange with defect accumulation processes in the ordered medium. We observed a similar situation in *PbTe-Bi₂Te₃* system in the composition range up to ~ 3 mol.% *Bi₂Te₃*, namely concentration dependences of σ , R_H , μ_H , as well as $\Delta B/B$ were of oscillatory nature [12]. And this situation is not unique. There are well known nonstoichiometric phases of variable composition where homogeneity area is divided into a number of subareas with different type of long-range or short-range ordering and very close compositions.

The initial growth of R_H on the introduction of the first portions of *PbSe* – up to 0.2 mol.%

(Fig. 4, *e*) can be related to a complex mechanism of defects formation occurring in this case. The point is that with a small content of impurity atoms a change in free energy is caused mainly by entropy member, and the probability of processes related to configuration entropy growth is increased, stimulating such phenomena as delocalization of impurity atoms with respect to the main structural positions (for instance, their introduction to interstitial sites), formation of new defect types, etc. On introducing selenium impurity atoms into interstitial sites of anion sublattice, chalcogen atoms create equivalent number of once ionized vacancies exhibiting donor properties. Moreover, it should be taken into account that on introducing the first portions of impurity atoms, because of a change in the thermodynamic equilibrium conditions in a doped crystal there can be a change in the equilibrium concentration of nonstoichiometric cation vacancies possessing acceptor properties, leading to a reduction of hole concentration and, respectively, to growth of R_H . Subsequent reduction of R_H with increasing content of *PbSe* to ~ 0.75 mol.% is in good agreement with the reduction of the Seebeck coefficient (Fig. 4, *e*).

Processes of impurity atoms redistribution with increase in impurity concentration can include: 1) formation of superstructure with a periodic distribution of impurity atoms in the structure of basic material; 2) formation of structure with short-range ordering extending to one or several coordination spheres; 3) change in the character of impurity atoms localization; 4) formation of clusters whose structure is different from the structure of basic material.

A qualitative change in properties can be expected, when with increasing concentration of doping component the average distances between impurity atoms achieve the values whereby their interaction covers the entire crystal, stimulating self-organization processes leading to a reduction of the internal crystal energy and assuring solid solution stabilization. It can be assumed that formation of percolation channels through *Se* impurity atoms on achievement of percolation threshold stimulates self-organization processes or is attended with them. Note that the value $r_0 \approx 1.5 a_0$ corresponds to close packing of impurity spheres with formation of face-centered cubic lattice with unit cell parameter $a = 4 a_0$.

In heterovalent nonisotstructural solid solutions between two chemical compounds after formation of “impurity continuum” there is high chance of short-range ordering of solid solution with formation in the initial compound of complexes with crystal structure different from die structure and corresponding to second component structure. As regards isovalent and isotstructural solid solutions, including *PbTe-PbSe* solution, here the probability of long-range ordering is higher.

Thus, the results of this work provide another evidence of the universal character of critical phenomena attending a transition from weak doping to formation of impurity continuum and governing a complicated character of the concentration dependences of properties. Irrespective of the character of interaction between impurity atoms, crystal properties are fundamentally changed, when a continuous chain of interactions between impurity atoms is formed and the velocity of distribution of elementary excitations is varied. Moreover, the results obtained imply that the emergence of percolation channels in a solid solution initiates self-organization processes in a solid solution leading to complex concentration dependences of properties.

Conclusions

Dependences of structural, mechanical, galvanomagnetic and thermoelectric properties on the composition of isovalent and isostructural solid solutions *PbTe-PbSe* in the range of concentrations 0 – 5 mol.% *PbSe* exhibit a distinct nonmonotonous character. The observed concentration anomalies

are proved by the fact of existence of percolation-type phase transition within any solid solution and testify to a complicated character of isotherms of properties in the transition area of concentrations between the dilute and concentrated solid solutions close to percolation area.

The obtained results should be taken into account in the investigation and interpretation of properties of solid solutions *PbTe-PbSe*, at their further doping for the purpose of optimization of thermoelectric parameters, as well as in the development of new thermoelectric materials based on lead telluride and other materials, as long as the discovered effects are, apparently, of a general nature.

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