

# Effect of heat treatment on the manifestation of a percolation phase transition in the semiconductor $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ solid solutions

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Investigation establish the influence of the technology of preparation and aging of the  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  solid solutions ( $0 < x \leq 0.09$ ) on the manifestation of a percolation-type concentration-dependent phase transition associated with the formation of impurity continuum. The room-temperature dependences of microhardness  $H$ , electrical conductivity  $\sigma$  and the Seebeck coefficient  $S$  on the alloy composition after different types of heat treatment as well as after long-term aging of the alloys. In all cases, concentration-dependent anomalies in the region  $x = 0.015-0.03$  were observed, indicating the presence of a percolation transition, but the nature of the anomalies was different. The obtained  $H(x)$ ,  $\sigma(x)$  and  $S(x)$  dependences are interpreted taking into consideration the influence of time and temperature factors on the diffusion processes occurring in the system, the concentration of intrinsic and impurity defects, and the percolation threshold.

**Keywords:**  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  solid solutions, percolation phase transition, heat treatment, aging, microhardness, electrical conductivity, Seebeck coefficient.

**Вплив термічної обробки на проявлення перколяційного фазового переходу в напівпровідникових твердих розчинах  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ .** *Г.О.Ніколаєнко, О.І.Рогачова, О.М.Нащекіна, Г.В.Лісачук*

Вивчено для твердих розчинів  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  ( $0 < x \leq 0.09$ ) вплив технології приготування та старіння на проявлення концентраційного фазового переходу перколяційного типу, пов'язаного з переходом до домішкового континууму. За кімнатної температури були одержані залежності мікротвердості  $H$ , електропровідності  $\sigma$  та коефіцієнта Зеебека  $S$  від складу після різних типів термічної обробки, яким піддавалися синтезовані зразки, а також після старіння сплавів за кімнатної температури. Встановлено, що концентраційні аномалії спостерігаються після усіх типів термічної обробки, вказуючи на присутність перколяційного переходу, але характер аномалій залежить від типу термообробки, яка використовувалася. Одержані залежності  $H(x)$ ,  $\sigma(x)$  та  $S(x)$  інтерпретовані, враховуючи вплив часових та температурних факторів на ступінь реалізації дифузійних процесів в системі, концентрації власних та домішкових дефектів та значення порога перколяції.

## 1. Introduction

Narrow-gap semiconductors  $\text{PbTe}$  and  $\text{SnTe}$  form a continuous series of substitutional solid solutions  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  with a NaCl-type lattice in the entire range of temperatures and compositions [1, 2]. These alloys are well known as materials widely ap-

plied in IR photodetectors, thermoelectric (TE) converters and other devices [2–4]. It determines the need for studying the dependences of the structure and physical properties (optical, thermoelectric, etc.) on the composition of the  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  solid solutions. The existence of gapless states and band inversions [2, 3] in certain composi-

tion ranges of this system, and the recent discovery of properties inherent in topological crystalline insulators [5] stimulate further work in this direction.

It is known that in  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  alloys, the concentration of the cationic vacancies and charge carriers (holes) increases with increasing  $x$ , and this leads to a monotonic decrease in the Seebeck coefficient  $S$  and an increase in electrical conductivity  $\sigma$  [1–4, 6]. According to [1, 6–8], the microhardness  $H$  changes monotonically along a curve with a slight maximum near  $x = 0.3$ . However, the authors of [9], who studied  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  samples prepared by ampoule method and subjected to long-term annealing, observed an anomalous drop in  $H$  with  $x$  increasing in the range of  $x = 0.015$ – $0.03$ , and attributed this effect to an increase in the deformation interaction between impurity atoms (IAS) when  $x$  increases. At low IAS concentrations, the elastic strain fields created by IAS are isolated from each other, but at a certain  $x$  they begin to overlap, which leads to a drop in  $H$  due to the partial compensation of elastic stresses.

By now, concentration anomalies of properties in the range of low impurity content have been found in many semiconductor and semimetallic solid solutions (see, for example, [10–13]), and have been attributed to the presence of a percolation-type [14, 15] phase transition (PT) from dilute to concentrated solid solutions, which is accompanied by critical phenomena [16–18]. To provide additional support to this assumption, detailed experimental studies are needed to observe the PT manifestation for different properties in different systems, to give their theoretical interpretation and to identify common patterns and specific features for different objects under study. One of the most important questions is how stable this effect is and whether it is the result of the incompleteness of diffusion processes when the concentration of IAS is low. The answer to this question is important not only from a scientific but also from a practical point of view, since most of the materials used for practical applications are solid solutions in a narrow (doping) or wide range of concentrations.

The goal of the present work is to find out how the manifestation of the observed in [9] effect for  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  alloys, specifically an anomalous decrease in  $H$  in a certain range of compositions, depend on the sample preparation technology and long-term aging at room temperature, and

whether similar anomalies can be observed in the concentration dependences of other properties.

## 2. Experimental

All samples of  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  solid solutions in the range  $0 < x < 0.09$  were obtained from high-purity elements (at least 99.999 % of the main component) by fusing them in quartz ampoules evacuated to  $10^{-3}$  Pa, using vibrational mixing. The objects of the study were polycrystalline samples prepared in three ways: 1) after being held at 1300 K for 5 hours, the melt was quickly cooled down to 820 K, kept at this temperature for 200 hours, and then cooled in air to room temperature (M1); 2) after being held at 1300 K for 5 hours, the melt was slowly cooled down to 820 K, held at this temperature for 500 hours, and cooled to room temperature in the turned off furnace (M2) [9]; 3) the samples obtained by method M2 were subjected to aging at room temperature for 25 years (M3).  $H$  measurements were carried out using a PMT-3 tester with a diamond pyramid at a load of 0.49 N and an indentation time of 10 s. The loading device was adjusted on fresh cleavages of NaCl single crystals.  $H$  for each sample was determined by measuring 30 indenter impressions and statistical processing of the experimental results.  $S$  was measured by the compensation method relative to Cu electrodes at a temperature difference between the hot and cold electrodes of 10 K at 30 points throughout the sample. The relative root-mean-square error in determining  $H$  and  $S$  did not exceed  $\pm 3$  %.  $\sigma$  was measured by the four-probe method with an error of  $\pm 5$  %. The measurement procedure for  $H$  was identical to that used in [9]. All measurements were carried out at room temperature.

## 3. Results and discussion

Fig. 1 shows the results of measuring  $H$  on samples obtained by three different methods (further, for simplicity, we will designate them as M1, M2 and M3 samples). In all three cases, there is a tendency for  $H$  to increase with increasing  $x$ , which is typical for solid solutions. Within the framework of the dislocation theory, the main mechanism of solid solution strengthening is associated with the elastic interaction of the fields of dislocations and IAS, leading to a decrease in the dislocation mobility and, consequently, an increase in  $H$  [19, 20].

Comparing the  $H(x)$  dependences obtained for the samples M2 and M3, one can see that a decrease in  $H$  in the range  $x = 0.015\text{--}0.03$  is observed in both curves and cannot be explained in terms of solid solution strengthening. As noted above, in [9], this effect was interpreted as the manifestation of the interaction between IAS, which, at a certain concentration, begins to spread over the entire crystal. By now we have observed similar concentration anomalies of various properties for various solid solutions and interpreted them in terms of percolation concepts [10–18]. Comparing curves 2 and 3, one can see that after keeping the samples for a long time at room temperature in air the position of the peak did not change, and curves practically coincide within the measurement error of  $H$ . This means that after M2, a fairly stable state is established, which practically does not change in terms of strength properties. However, one can also see some differences between the  $H(x)$  curves after M2 and M3: 1) the peak width becomes somewhat narrower after aging (the drop in  $H$  continues not to  $x = 0.03$ , but to  $x = 0.025$ ), i.e., the percolation transition occurs in a narrower concentration range; 2) the intensity of the peak (relative amplitude value) after M3 increases from 22 % for M2 to 38 %); 3) after M3, the  $H(x)$  dependence in the composition range  $x = 0.04\text{--}0.07$  revealed a plateau section, which is very weakly expressed for the M2 samples in the composition range  $x = 0.06\text{--}0.07$ .

On the other hand, there are significant differences between curves for M2 and M3 and that for M1. First, for M1 instead of a distinct single peak near  $x = 0.015$ , the peak splitting is observed. Such non-monotonic behavior of the dependence can be associated with the fact that after heat treatment M1, the system does not come to an equilibrium state. With the insufficient annealing time and rapid cooling rate, an additional peak at  $x = 0.005$  appears in the  $H(x)$  dependence before the percolation peak. We associate its appearance with a nonequilibrium state of the solid solution when the first portions of IAS are introduced, characterized by the presence of nonequilibrium defects (e.g., interstitial atoms). At a low impurity content, the entropy factor plays an important role, and thus, the probability of the formation of nonequilibrium defects, for example, IAS in interstices, is high. Then, as a certain amount of IAS is introduced, stresses in the

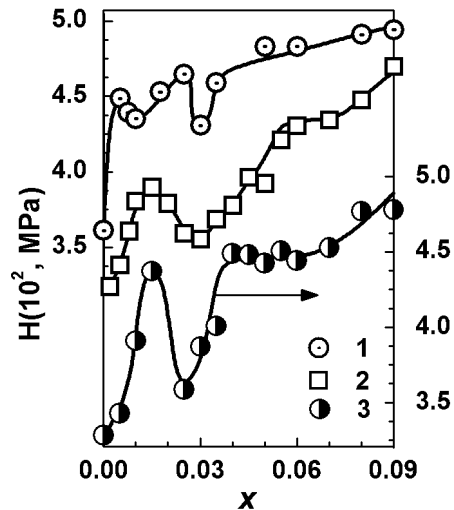


Fig. 1. The dependences of microhardness  $H$  of the  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  solid solutions prepared by different methods: (1) the melt was rapidly cooled to 820 K, kept at this temperature for 200 hours, and cooled in air (M1); (2) the melt was slowly cooled to a temperature of 820 K, kept at this temperature for 500 hours, and cooled at the rate of the furnace turned off; (3) after M2, the samples were aged at room temperature for 25 years.

system are relaxed and, possibly, the interstitial atoms take their regular positions. After that,  $H$  increases again due to solid solution strengthening, reaches the percolation threshold  $x_c$ , and falls. It can be seen that  $x_c$  shifts towards higher  $x$  compared to samples M2 and M3.

In Fig. 2a, the  $\sigma(x)$  dependence is shown for the same M1 samples. Electrical conductivity depends not only on charge carrier concentration  $n$ , but also on carrier mobility  $\mu$  ( $\sigma = n \cdot e \cdot \mu$ ), which, in turn, depends significantly on the stresses in the crystal lattice created by IAS. This leads to the non-monotonic behavior of the dependence of  $\sigma$  on the composition, especially in the region of low impurity concentrations, because  $n$  and  $\mu$  depend on the composition in different ways, often in the opposite way. The situation becomes more complicated under the action of kinetic factors when the system is far from an equilibrium.

The  $\sigma(x)$  dependence for M1 samples is in a good agreement with the  $H(x)$  dependence. Indeed, the sharp drop in  $\sigma$ , which indicates a decrease in  $\mu$  with the introduction of the first portions of Sn, corresponds to a sharp increase in  $H$ , additionally indicating the appearance of the excess number of defects

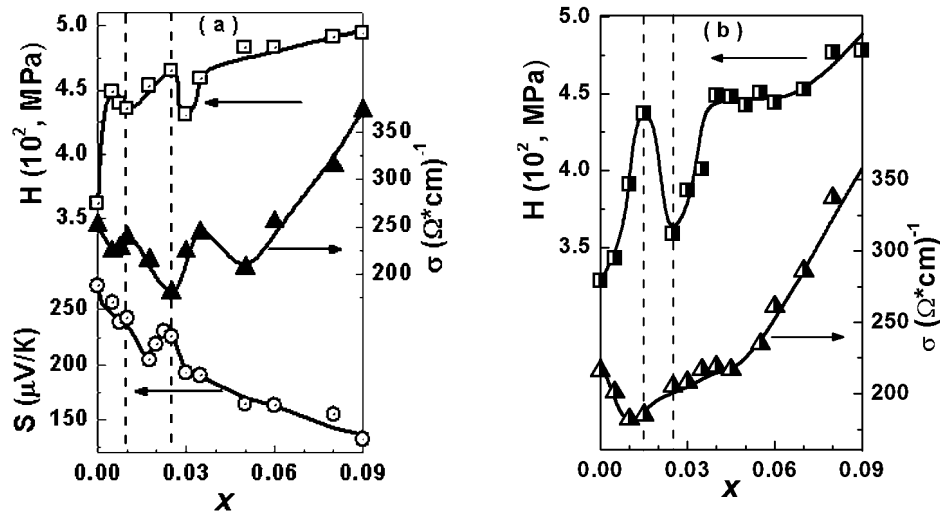


Fig. 2. (a): The concentration dependences of microhardness  $H$ , electrical conductivity  $\sigma$ , and the Seebeck coefficient  $S$  of the  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  solid solutions prepared by the M1 method. (b): the  $H(x)$  and  $\sigma(x)$  dependences for the samples prepared by the M3 method (after M2, the samples were aged at room temperature for 25 years).

stimulated by the predominant contribution of the entropy factor to free energy, when the number of IAS is small. The subsequent increase in  $\sigma$  in the same narrow concentration range (up to  $x = 0.01$ ), where the drop in  $H$  is observed, is in good agreement with the assumption that the number of non-equilibrium defects can be partially reduced when the interstitial atoms return to their regular positions. A further increase in  $x$  leads again to an increase in  $H$  and a decrease in  $\sigma$  until the system reaches a state where the interaction of IAS becomes collective, and the percolation threshold  $x_c$  is reached. This occurs near  $x = 0.025$ , but not near  $x = 0.015$  like for samples M2 and M3, i.e., the expected percolation threshold for samples in a non-equilibrium state is reached later.

For M3 samples, at  $x < x_c$ , when IAS act as individual scattering centers,  $\mu$  decreases most significantly, and it is this fact that determines the decrease in  $\sigma$  similar to that for M1 samples. However, for M3 samples increase in  $\sigma$  associated with non-equilibrium state of M1 samples, is absent (Fig. 2b). Upon reaching the percolation threshold at  $x = 0.015$ ,  $\mu$  and  $\sigma$  increase because of the formation of percolation channels. However, after the system has passed into the state which we call "impurity continuum",  $\sigma$  does not fall again, like at  $x < x_c$ , but increases. This happens because although the carrier mobility should decrease as a result of the introduction of new por-

tions of IAS and the increased impurity scattering, but the increase in hole concentration when SnTe is introduced into PbTe (due to an increase in the number of cation vacancies) is more significant [1–4, 6].

Since isovalent substitution takes place in  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  solid solutions, the predominant type of the interaction between IAS is the deformation interaction associated with the lattice subsystem of the crystal and affecting primarily the mechanical properties, including  $H$ . At the same time,  $S$  depends mainly on carrier concentration  $n$ , that is, on the properties of the electronic subsystem of the crystal, which is less affected by the deformation interaction. Therefore, the processes of interaction between IAS, including percolation effects, have a weaker effect on the  $S(x)$  dependences and are not detected in M2 and M3 samples in which, in both cases,  $S$  decreases linearly with increasing  $x$ , as for M2 samples in [9]. However, for M3 samples,  $S$  values decrease by  $\sim 10\%$ , which corresponds to an increase in the hole concentration by  $\sim 20\%$ . This can be associated with the exposure of the samples in air without protective covering for 25 years. It is known that oxygen acts as an acceptor impurity in IV–VI crystals, and the surface adsorption of oxygen can significantly change the properties of crystals and especially of thin films [2, 21]. The appearance of a peak in the  $S(x)$  dependences for M1 samples that are far from equilibrium (Fig. 2a) can be associated with the action of kinetic factors. A significant de-

viation from equilibrium upon the introduction of the first portions of an impurity, supersaturation with defects lead to the fact that, at a certain  $x$ , the system relaxes and passes into a closer to equilibrium state.

The interaction between IAs, which spreads over the entire crystal after reaching the percolation threshold, stimulates the processes of redistribution of IAs over the crystal with the formation of configurations corresponding to the minimum of the thermodynamic potential. The plateau area in the  $H(x)$  dependence for M3 samples ( $x = 0.04-0.07$ ) indicates that during aging there is a partial compensation of the fields of elastic stresses of IAs. It can be assumed that because of self-organization processes (short- or long-range ordering, complex formation or solid solution decay) occurring in the crystal lattice, atomic configurations are formed that reduce the lattice deformation energy and do not cause a change in the hole concentration. It is possible that under conditions of long-term low-temperature annealing (for example, at 500 K), these processes will occur faster due to an increase in the diffusion rate and the manifestation of the processes occurring in the solid solution and associated with the formation of intermediate states will be clearer. The subsequent faster growth in  $\sigma$  at  $x > 0.04$  can be connected with relate to ongoing self-organization processes leading to an increase in  $\mu$  and, hence,  $\sigma$  (see above).

#### 4. Conclusions

1. An important factor determining the completion of the percolation phase transition in the  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  solid solutions is a duration of homogenizing annealing  $t_a$  and cooling rate  $v_c$ . An insufficient  $t_a$  and high  $v_c$  lead to: 1) a less clear manifestation of the percolation peak in the  $H(x)$  dependence; 2) a shift of the percolation threshold  $x_c$  towards higher  $x$  values; 3) the appearance of an additional peak in the  $H(x)$  and  $\sigma(x)$  dependences, associated with the non-equilibrium state upon the introduction of the first portions of IAs. An increase in  $t_a$  and a decrease in  $v_c$  lead to a more pronounced manifestation of the percolation peak and the absence of an additional peak.

2. Aging at room temperature for 25 years after 500-hour annealing do not change the  $H$  values and the position of the percolation peak in the  $H(x)$  curve but leads to a narrowing of the peak and twofold in-

crease in its relative intensity. At  $x > x_c$ , changes are observed in the  $H(x)$  and  $\sigma(x)$  dependences indicating self-organization processes in the solid solution.

3. After the prolonged annealing and aging, the  $S(x)$  dependences do not exhibit anomalies connected with the percolation transition. It can be explained by the fact that the main type of interaction between IAs in isovalent solid solutions is deformation interaction and changes in these interactions are reflected in the lattice properties, and not in the electronic ones.

The results obtained in this work show that concentration anomalies in the  $H(x)$  and  $\sigma(x)$  dependences for  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  alloys are not the result of a non-equilibrium state but indicate the existence of a phase transition of percolation type which takes place during the transition to the impurity continuum.

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