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PHASE DIAGRAMS OF THE $A^{IV}B^{VI}$ SEMICONDUCTING SYSTEMS – ADDITION (IMPURITY)

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The semiconducting compounds of the type $A^{IV}B^{VI}$ (Ge-Te, Sn-Te, etc.) with low amount of additions, at the impurity level, are discussed. The phase diagrams in various cases are shown and the influence of impurities on various properties of the semiconducting matrix is pointed out.,

The doping of the semiconducting compounds of type $A^{IV}B^{VI}$ is largely used as a method of controlled synthesis. Thus, it is possible not only to vary the composition, in particular the concentration of the free charge carriers, but also to create new properties in the initial material. The selection of this or that addition and the mode of introduction in the semiconductor $A^{IV}B^{VI}$ are determined by the position of the doping element in the Periodic Table, its solubility and coefficient of dopant distribution, by its volatility, by the character of the chemical interaction of the impurity atoms with the atoms of the semiconductor and, also, by the character of interaction of the impurity atoms with the structural defects. As impurities (additions) are used the metals of the group I (Na, Ag, Cu), of the group II (Zn, Cd), of the group II (Al, Ga, In, Tl) and of the group V (Sb, Bi) of the Periodic Table.

The problem of the doping of the semiconductors $A^{IV}B^{VI}$ is both complicated and multi-sided. The physico-chemical study of this problem allows to explain such important facts as controlled modification of the semiconductor properties and the preparation of new semiconducting materials. The works in this direction have extremely important value in relation to the problems of stability and reproducibility of the properties of the active elements in the devices that use doping semiconducting materials.

The resolving of the problems of semiconductor doping cannot be separated from the study of impurity electronic states that appear in semiconductors during doping. An important place is occupied by the research of the distribution coefficients, of the equilibrium between phases and the interaction of the components in the systems semiconductor-addition, and, also, the study of the solubility of the impurities in semiconductors for various conditions. The study of the solubility and character of its dependence on temperature allows to find correctly the possible limit of doping with different impurities, to understand those modifications of the semiconductor properties, which could appear during thermal processing of the doped semiconductors and in the process of its natural aging.

The establishing of the character of the heterogeneous equilibria in the systems semiconductor-impurity represents the basis of the doping and for its correct understanding it is necessary firstly to have the necessary quantitative data on the equilibrium between phases. Such data are given by the phase diagram of the system semiconductor – impurity. In principle there are not differences between the phase diagrams of the usual systems and the system semiconductor – impurity. The difference consists only in the form of their representation [1].

Because the solubility of the doping additions in the solid state semiconductors is low (usually under the limit $1 \div 2$ at.%), it is difficult to represent on the phase diagram the liquidus and solidus lines (surfaces). That is why for the representation of the solidus is used not a linear but a logarithmic scale. In the case of the systems semiconducting binary compound – impurity, the representation of the phase equilibria needs the construction of the ternary phase diagrams. For this, on the phase diagram of the technologist, firstly it is of interest the domain of primary crystallization of the semiconductor and the liquidus and solidus surfaces in this domain.

The construction of the liquidus curves is made by the usual method of thermal analysis. Nevertheless, the construction of the solidus curves and the limited solubility for the systems semiconducting compound – impurity cannot be achieved by thermal analysis, because the solid solution domains based on the semiconducting compounds are small, and this determines the absence of the corresponding thermal effects on thermograms. Therefore, one uses methods, based on melt quenching of the alloys semiconductor – impurity from the liquid state followed by annealing at well defined temperatures and quenching from those temperatures. Thereafter, the alloys are investigated by different physico-chemical methods (microstructural, X-ray diffraction, microhardness, density, etc…).

The crystallization of the doped semiconductors leads to the formation of the solid state solution, and the state of the doping additions depends on various causes, as e.g. the state of the crystallization medium, the crystallization conditions and thermal processing of the grown crystal [2,3]. The magnitude of the solubility is, in general, determined by the distortion of the chemical bond, introduced by the impurity atoms, that depends on chemical nature, size, localization and the state of the impurity atoms. The most important factor that controls the solubility of the impurity additions is the degree of similarity of the energetic characteristics of the valence electrons of the impurity atoms and those of the electrons of the atoms in the crystalline lattice that are substituted [2]. More largely these energetical characteristics differ, more difficult is to predict the reaction of the crystal on its doping, i.e. on the distribution of the doping atoms.

By the introduction in the crystalline lattice of the compound $A^{IV}B^{VI}$ of some element C as a binary compound $C_xB_y^{VI}$, it appears the possibility to get the dissolution along different sections of the ternary system A-B-C, that cross the compound $A^{IV}B^{VI}$ [3]. In this case, apart the element C (cation-forming), in the lattice additionally enters one of the components of the compound B (chalcogen) – anion-forming. For $x=y$ in the crystalline lattice of the compound $A^{IV}B^{VI}$ simultaneously enter the atoms of the elements C and B, i.e. the formation of the solid solutions is accompanied by the substitution $A \rightarrow C$. In this case the number of charge carriers, introduced by every atom of the element C is equal to the valence difference of A and C atoms. For favourable dimensions and vicin crystallo-chemical factors, the substitution solid solutions can have a significant concentration interval. For $x > y$ the solubility is connected with the action of a minimum two mechanisms (e.g. substitution and subtraction), and for $x < y$ the most probable is the formation of the solid solutions of subtraction character, with vacancies in the cation sublattice. For deviations of the composition of the compound $A^{IV}B^{VI}$ – dissolving medium from stoichiometric ratio of the components, there are possible mechanisms of dissolving, excepting those enumerated above, related to the vacancy filling, that take place in the initial compound.

In the next section we shall describe the most studied phase diagrams for the systems semiconducting $A^{IV}B^{VI}$ – impurity.

4.1 The solubility of the impurities in GeTe.

In the antimony chalcogenides the donor or acceptor behaviour of the impurity are conditioned, as normally, by its valence. Thus, in the antimony tellurides the atoms of the first group (Na, Ag, Cu) are, usually, acceptors and the elements of the fifth group (Sb, Bi) are donors. In spite of the fact that the germanium telluride belongs to the same type of compounds, due to the presence of germanium vacancies, it is possible to occur an other mechanism of formation of the current carriers during introduction of the above shown impurities. The impurity atoms must preferably occupy the vacant places in the cation sublattice, by giving their valence electrons to tellurium and thus, diminishing the general concentration of the holes.

The solubility of the impurities in vacancies essentially depends on the vacancy concentration in the initial material. This is evident from the comparison of the influence of various impurities on the concentration of the current carriers during their introduction in the GeTe and $Ge_{0.97}Te$ alloy. The increase of the vacancy number in GeTe leads to the increase in solubility: for copper from 2 to 3 %, for bismuth from 0.4 to 1.5 at. % [4]. The solubility in vacancies depends, also, on the size of the impurity atoms. In GeTe, having unique initial vacancy concentration, copper dissolves in large limits, than bismuth (the covalent radii of copper and bismuth are 1.39 and 1.50 Å, respectively). In the same time the solubility of the impurities in vacancies is limited and always smaller that the vacancy concentration. In the presence of the free vacancies it is possible the dissolution of the Cu, Sb, and Bi impurity in significant amounts by substitution of germanium in the occupied sites of the lattice, similarly to the dissolution mechanism of the impurities in lead chalcogenides. In this case the change of the carrier concentration is determined by the ratio of the germanium valency to Sb and Bi valency.

The compound Cu_2Te and elementary copper are well known dopants of donor type in germanium telluride, that are used for diminishing of the hole concentration. The solubility of the elementary copper in germanium telluride after homogenizing firing at 820 K for 600 h is 1.5 at.% [4]. X-ray diffraction investigation of the alloys in the system GeTe-Cu has shown that all alloys exhibit the α-phase with rhombohedral symmetry and is observed a small increase of the lattice parameter and volume of the elementary cell.

The investigation of the dependence of the concentration of the charge carriers on the concentration of the introduced atoms of the elementary copper has shown that the decrease of the hole concentration is related to the dissolution of copper in the vacancies situated in the cation sublattice GeTe [5]. In this case, there was established that every copper atom diminishes the hole concentration by two units, and on this basis it was concluded that copper in germanium telluride is di-valent. Nevertheless, the X-ray photoelectron spectroscopy (XPS) [4] did not supported this conclusion, and has shown that copper in GeTe takes a single-valency state. By dissolving in vacancies, every copper atom, in this case, decreases the hole concentration by one unit. Nevertheless, the decrease by 4.5×10^{20} cm^{-3} of the hole concentration, observed experimentally, overcomes the concentration of germanium vacancies, filled by copper atoms. Because every non-stoichiometric vacancy is double ionized, the authors of [4] stimated the concentration of vacancies filled by copper as the difference between the concentration of the vacancies in the initial GeTe ($[V_{Ge}]_{in} = ½ P_{in} = 3.2 \times 10^{20}$ cm^{-3}) and the vacancy concentration remained after doping ($[V_{Ge}]_{fin} = ½ P_{fin} = 1.0 \times 10^{20}$ cm^{-3}). From this follows that the vacancies filled by copper, in single-valent state, can be explained by the diminishing of the hole concentration only by $\sim 2.2 \times 10^{20}$ cm^{-3} , i.e. around a half of general decrease of the hole concentration observed at doping. The remaining part of the decrease of the hole concentration has been related by the authors of [4] with the placing of copper in interstices, because thus copper, too, shows donor effect. Because the concentration of the dissolved copper atoms for the given thermal processing is $N_{Cu} \sim 5.8 \times 10^{20}$ cm^{-3}, the experimentally observed dependence of the hole concentration on the copper content in GeTe is well explained in the hypothesis that ~ 40 % of the copper atoms fill the vacancies in the cation sublattice, the same percent are placed in the interstices and ~20 % of copper remain neutral. The observation of the increase of the Hall hole mobility is also related to the filling of the cation vacancies by copper atoms [4].

The single valent state of copper in the solid solutions GeTe-Cu can be, also, estimated by the analysis of the causes of the appearance on the curves of temperature dependence of the electro-physical properties, of sharp anomalies in the domain of phase transition $\alpha \rightarrow \beta$, evidenced in [6]. The explanation of the appearance of these anomalies is given, starting from the supposition that copper transforms from the di-valent state to single-valent state during transformation in the cubic phase, that determines the weakening of its donor state. This explanation does not agree with the photoelectrical spectroscopy data, according to whom copper, already in the low-temperature rhombohedral phase, is in single-valent state. The possible cause of the increase of the hole concentration by phase transition, as considered by the authors of [4] [313] is the change of the character of the introduction of the copper atoms in the lattice of germanium telluride during transformation in the cubic phase. The copper is an impurity that diffuses easily in the germanium telluride and, evidently, easier than other elements copper can change its position in the GeTe lattice with the increase of the temperature.

The phase diagram of the system $Ge_{0.975}Te$-Cu_2Te and the influence of the compound Cu_2Te on the hole concentration in germanium telluride with deviation from stoichiometry are studied in [7], where the authors have shown that the solubility boundary of Cu_2Te in germanium telluride at 838 K is situated between 3 and 5 mol.%. The boundary of the solubility domain changes as a function of the temperature of the thermal processing (Fig. 4.1). After firing at 853 K the domain of the solid solutions increases within the triangle along the section $Ge_{0.97}Te$-Cu_2Te up to 3 at. % Cu and extends in the concentration limits 51 ÷ 49.5 at.% Te (Fig. 4.1 a). The annealing at 573 K leads to the narrowing of the domain of solid state solutions. The solubility limit of copper in germanium telluride at 573 K is ~2.5 at. % (Fig. 4.1 b).

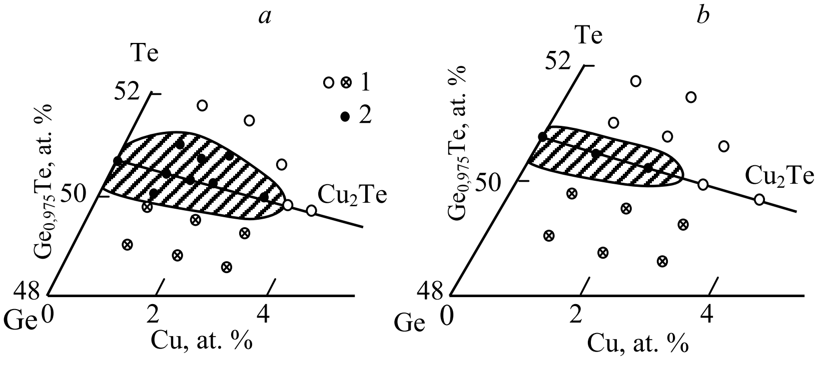

Fig. 4.1 The domain of solid solution of copper in $Ge_{0.97}Te$ [7]. After firing at 853 K (a) and 573 K (b). Alloys: 1 – di-phasic, 2 – single phase

By doping of the germanium telluride with the compound Cu_2Te one observes a smaller diminishing of the hole concentration, than it is produced in the case of GeTe doping with elementary copper. Cu_2Te shows in GeTe a weak donor property: the introduction of ten copper atoms lowers the hole concentration by two units. The authors of [4] consider that the Cu_2Te molecules enter into the GeTe lattice mainly as electro-neutral complexes with the formation of one anion vacancy for every Cu_2Te molecule. These conclusions agree with the results of lattice parameter determination for the elementary cell, which, practically, do not change during dissolving of Cu_2Te in germanium telluride.

Excepting the interstitial introduction as electro-neutral complexes, some amount of copper, introduced by dissolving Cu_2Te in GeTe, can fill the non-stoichiometric cation vacancies, which are the dominant defects in the rhombohedral low temperature phase in GeTe. In the solid solution of the system GeTe-Cu_2Te is achieved the equilibrium between the copper atoms, that enters into the electro-neutral complexes and the copper atoms that dissolve in the non-stoichiometric cation vacancies. By increasing the vacancy concentration on the account of the deviation from stoichiometry on the tellurium side, the equilibrium shifts on the side of increasing number of copper atoms, filling up the vacancies and exhibiting donor properties. That is why, in [7], where the composition germanium telluride $Ge_{0.975}Te$ has been doped by Cu_2Te, the authors observed a more essential diminishing of the hole concentration as compared to doped stoichiometric GeTe.

The elements of the III b subgroup Al, Ga and In introduced in the compounds $A^{IV}B^{VI}$ exhibit donor properties in spite of the presence of the lower amount of valence electrons. This is due to the fact that the doping with the elements of the III b subgroup is related to two localization positions for the impurity atom in the crystalline lattice of the compound $A^{IV}B^{VI}$. Part of the doping atoms is distributed on the lattice sites in the positions of Pb, Ge and Sn. In this case the impurity atoms exhibit acceptor properties (due to lower amount of valence electrons).

On the basis of microstructural and X-ray diffraction analyses, and, also, by the measurement of the microhardness and density as a function of composition [8] it was determined the solubility limits of the components in the systems GeTe-GaTe and GeTe-Ge_2Te_3 up to 7 and 5 mol. % of the second component. Nevertheless, these data have not found support in the following researches [9, 10] of the corresponding phase diagrams. By considering the deviation from stoichiometry in germanium mono-telluride [9, 10] it has been studied the phase diagram along the cross-section $Ge_{0.975}Te$-Ga_2Te_3. The investigated cross-section of the ternary system Ge-Ga-Te is a pseudo-binary section; the phase diagram of the system $Ge_{0.975}Te$-Ga_2Te_3 is of eutectic type with limited solubility of the components in the solid state. At 873 K the homogeneity domain based on germanium mono-telluride does not overcome 0.5 mol. % according to [9] [318] and extends toward 2 mol. % Ga_2Te_3 after the data reported in [10,11] (Fig. 4.2). When the temperature decreases down to 573 K the solubility domain becomes narrower. For the concentration of Ga_2Te_3 in $Ge_{0.975}Te$

above 2 mol. %, on the borders of particles does appear the second phase – Ga_2Te_3, whose amount increases with the increase of the Ga_2Te_3 content.

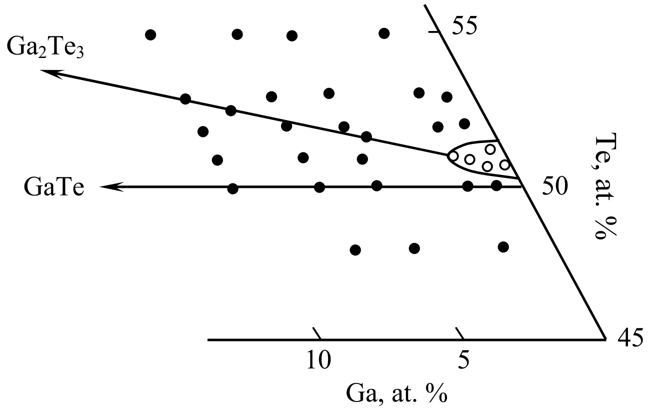

Fig. 4.2 The domain of solid solutions of Gallium in GeTe at 873 K[11].

X-ray diffraction analyses of the alloys in the domain of solid solutions have shown that the substitution of germanium by gallium does not induce the change of the crystalline structure of the germanium telluride, but it remains rhombohedral. A not significant decrease of the volume of the elementary cell, observed in the solid solution $Ge_{0.975}Te$-Ga_2Te_3, according to [11] [320], indicates that by the formation of the solid solution the vacancy mechanism of dissolution of tellurium, characteristic to GeTe, is preserved. The increase of the lattice thermal conductivity and mobility in solid solution influence the decrease of the number of vacancies in the $Ge_{0.975}Te$ lattice, which are centers of thermal scattering. An observed sharp change in the concentration of the charge carriers, the increase of mobility and thermal conductivity at doping of the germanium mono-telluride with Ga_2Te_3, indicate the special dissolving mechanism of Ga_2Te_3 in the GeTe lattice, which is manifested by the more rapid filling of vacancies in the GeTe crystalline lattice not only by Ga but also by Te [11] [320].

In Fig. 4.3 are given the isothermal lines of solubility in the system Ge-In-Te for various temperatures. From the solubility isotherms it is evident that in the concentration triangle do exist directions, along those the solubility is essentially higher than that obtained from the additivity rule. The maximum values of the solubility corresponds to the cross-sections that pass through the congruently-melting compound InTe or In_2Te_3 and corresponding formation of substitutional solid solutions (in the case of the GeTe – In_2Te_3 section the substitutional elements are the stoichiometric vacancies) [12]. The comparison of the radius of the cation of the dissolving medium (Ge) and the average cation radius of the substitutional complex shows that for the alloys based on GeTe the dimension factor is mostly convenient along the section GeTe-In_2Te_3 ($\Delta r/r \approx 5\%$). The orientation of the homogeneity domain of GeTe in the system Ge-In-Te along the cross-section GeTe-In_2Te_3 [12], i.e. the shift of the boundaries of the homogeneity domain on the side of increasing Te content, corresponds with donor properties of indium in the given system and indicates the increase of the limit of the content of cationic vacancies by introducing indium.

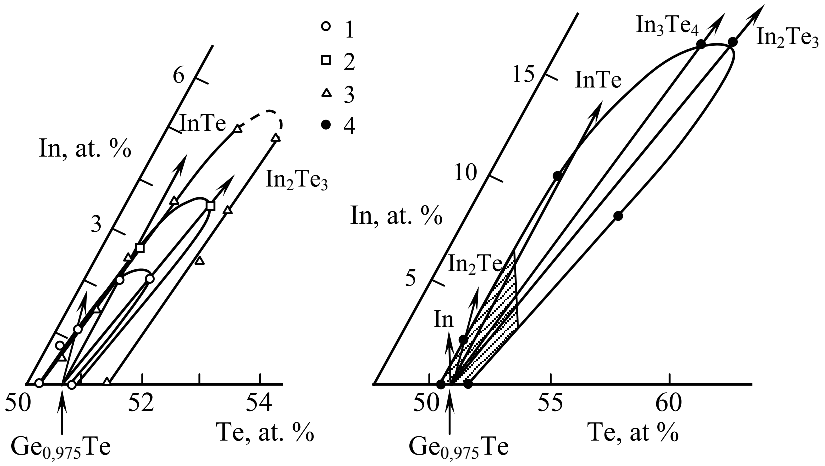

Fig. 4.3 Solubility isotherms in the system Ge-In-Te[12]. 1 – 473; 2 – 573; 3 – 673; 4, 5 – 823 K. The hatched zone represent the domain of existence of the rhombohedral phase.

The direction of the solubility determines the scheme of substitution, consequently, the mechanism of formation of solid solutions. For example, along the section $Ge_{0.975}Te$-InTe it is most probable the formation of substitutional solid solutions (Ge → In), and along the section $Ge_{0.975}Te$-In_2Te_3 the most probable is the formation of solid solutions substitutional – subtraction (3Ge → 2 In + □, where □ is a neutral vacancy) [12]. The neutral vacancies change the density of the electronic charge and are sources of supplementary gradients of electric field on the tellurium nuclei, that are evidenced in higher velocity of the change of the parameters of the Mössbauer spectra, as for $Ge_{0.975}Te$-In_2Te_3 alloys. Along the section $Ge_{0.975}Te$-In_2Te_3, in the crystalline lattice are introduced an excess number of of cations (Ge-2In), whose most probable localization is the charged vacancies that exist in the lattice of the dissolving medium.

The fundamental mechanism of formation of the solid solutions along the section GeTe-In is the filling of the Ge vacancies by indium atoms, and every indium atom diminishes the hole concentration by three units, showing normal valency [5]. After the slope of the line describing the dependence of the charge carriers on composition, there was established [13] that by formation of solid solutions along the section GeTe-InTe the indium atom, which substitutes the di-valent germanium, decreases the hole concentration by one unit. In the alloys GeTe-In_2Te_3 the sums of the valencies of substitutional atoms are equal, so that the carrier concentration must exhibit modifications with composition [3, 13].

A peculiarity of the alloys GeTe-InTe and GeTe-In_2Te_3 is the inversion of the sign of the conductivity by introduction of more than ~6 at.% Indium in the crystalline lattice. By exhibiting donor properties, indium diminishes the carrier concentration of p-type; as a result, for the given composition is produced the transition toward the electron conductivity. Along the section GeTe-In_2Te_3 the conductivity remains by holes, because the change 3Ge → 2In is isovalent [3].

The system Ge-Sb-Te has been studied in [14, 16] along two sections GeTe-SbTe and GeTe-Sb_2Te_3. The solid solution domain along the section GeTe-Sb_2Te_3 extends up to 5 ÷ 7 mol.%, as a function of the annealing temperature. On the Fig. 4.4 it is shown the domain of existence of the solid solutions on the side of GeTe based on the microstructural data. The highest solubility of Sb (7.5 at. % at 873 K) is obtained along the section $Ge_{0.975}Te$-Sb_2Te_3. When the temperature decreases the solubility diminishes and at 523 K becomes ~1 at.% Sb. The adding of Sb in GeTe (the same case is Bi) leads to the stabilization of the cubical lattice of germanium telluride at room temperature [15]. The change of the density and number of atoms in the elementary cell of the solid solution Sb_2Te_3 in $Ge_{0.975}Te$ indicates that in the system take place not only the process of substitution of the germanium by antimony, but also the filling of the vacancies in the germanium sublattice. The authors of [324] suppose that in solid solutions take place two processes: a) the dissociation of Sb_2Te_3 in Sb_2Te_2 and Te and the filling with the neutral Te atoms of the vacancies in the GeTe sublattice; b) the formation of new vacancies on the account of further dissolution of Sb_2Te_3 in GeTe.

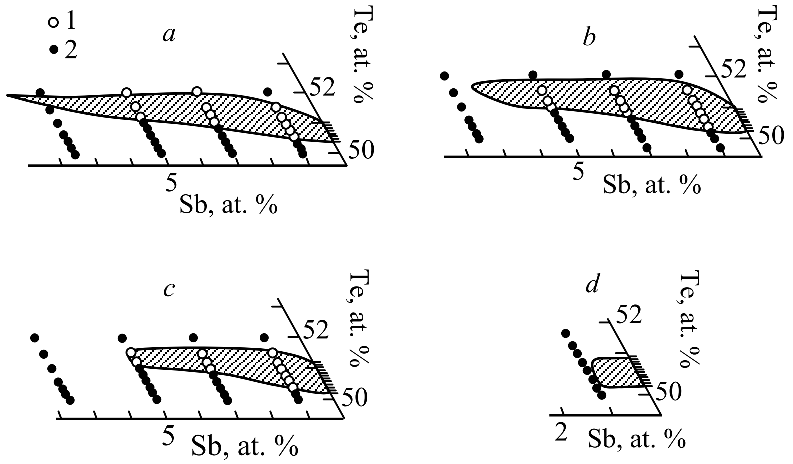

Fig. 4.4 The domain of solid solutions of Sb in GeTe [15] at 873 K; b) at 773 K; c) at 673 K; d) at 523 K; 1 – single phase sample; 2 – two phase sample.

By doping with antimony one observes the increase of the experimental density above that determined by X-ray diffraction, and the number of atoms in the elementary cell overcomes the theoretical number 8, and these facts indicates the placing of the atoms in interstices. This speaks in favour of the presence of antistructural defects; the substitution of tellurium atoms by antimony in the germanium sublattice and the placing of the Sb atoms in interstices [15].

The research on the limits of solubility of Te in the solid solutions of the system GeTe-Sb_2Te_3 has shown [13] that the dependence of the Hall concentration of the charge carriers $p_X(x)$, on the amount of the second component coincides with the analogous dependence for GeTe, and the homogeneity boundary shifts during the increase of the Sb_2Te_3 concentration on the side of decrease of the Te content in the alloy.

By doping GeTe with Bi, the placing of the atoms in the interstices is not observed because of the large size of bismuth atom. In the papers [17-21] were reported observations of the donor properties of Bi, BiTe and Bi_2Te_3 during their dissolution in GeTe. Bismuth can dissolve in GeTe in two modes: at concentrations < 1 at. % mainly in the germanium vacancies and for concentrations > 1 at.% mainly by substituting germanium Fig. 4.5 shows the solubility isotherm in the system Ge-Bi-Te. The increase of the Bi content up to 0.5 at.% sharply shifts the boundary of the homogeneity domain GeTe from the side of Ge to the side of increasing content of Te (from ~50.3 in the system Ge-Te up to 50.6 at.% Te at 0.5 at.% Bi), after that this shift is less significant; the boundaries of the homogeneity domain on the side of tellurium shift monotonously toward the side of the increase of Te content. During the investigation of the boundaries of the homogeneity domain of GeTe in the system Ge-Bi-Te for various temperatures it was established [17] that the maximum solubility corresponds to the section $Ge_{0.975}Te$-Bi_2Te_3 and comprises ~6.8 at.% Bi at 820 K and 4.2 at.% Bi at 770 K.

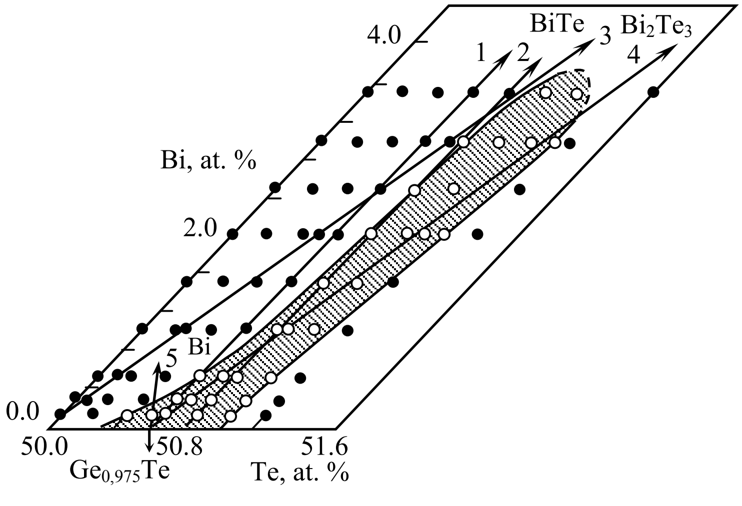

Fig. 4.5 Solubility isotherm in the system Ge-Bi-Te at 1043 K [19].

The increase of the Te content at constant concentration of Bi leads to the increase of microhardness H and concentration of the charge carriers p_x (Fig. 4.6). The authors of [19] relate these facts to the increase of the cation vacancies that are centers of distortion of the crystalline lattice and sources of free charge carriers (holes).

Along all the radial sections (Fig. 4.7) it is possible to separate a domain of low Bi concentrations (up to ~1 at.%) and in this limit the properties of the samples changes differently than in the remaining domain of compositions. Introduction of the first Bi_2Te_3 molecules both in GeTe and $Ge_{0.975}Te$ diminishes the hole concentration p_x, and in both cases every impurity atom gives ~1 current carrier. By introducing Bi_2Te_3 two processes take place [19] [328]: the substitution Ge → Bi and the introduction of excess Te.

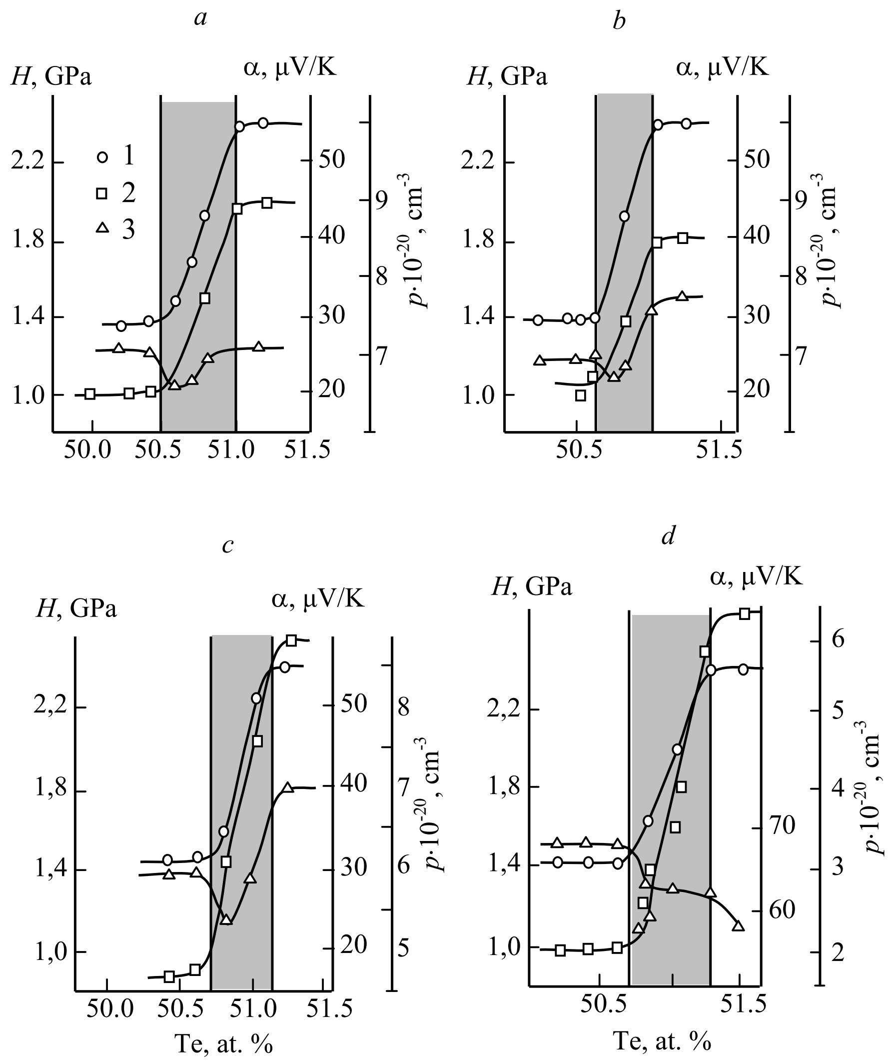

Fig. 4.6 The dependence of microhardness H(1), of charge carrier concentration p_x(2) and of the coefficient of thermo-electromotive force α (3) on the Te content along the iso-concentration line: Bi 0.25 (a), 0.5 (b), 1 (c), 3 at.% Bi (d) in the system Ge-Bi-Te [19].

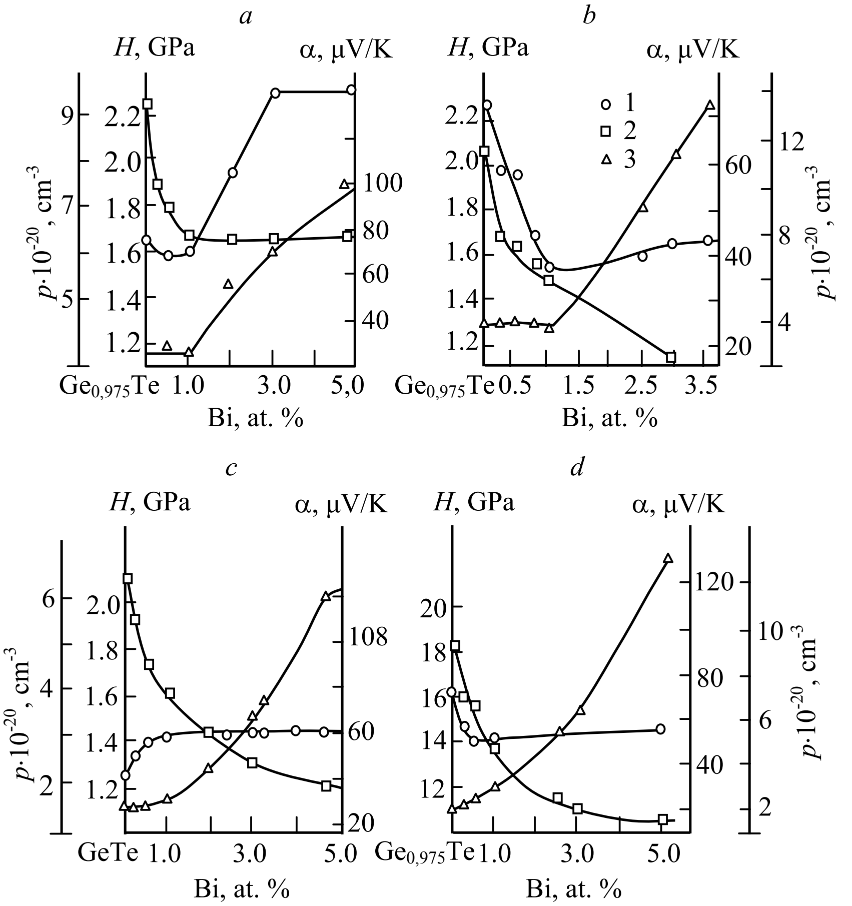

Fig. 4.7 The dependence of microhardness H(1), of charge carrier concentration p_x(2) and of the coefficient of thermo-electromotive force α (3) on the Bi content along the radial sections: $Ge_{0.975}Te$-Bi_2Te_3 (a), $Ge_{0.969}Te$-BiTe (b), GeTe-Bi_2Te_3 (c), $Ge_{0.975}Te$-BiTe (d) in the system Ge-Bi-Te [19].

If by substitution Ge→Bi every Bi atom gives one carrier in the conduction band (considering the valence of Ge and Bi), and every excess Te atom by changing the anion sublattice and creating an equivalent quantity of vacancies (two holes in the valence band), then, as a whole, the Bi_2Te_3 must be neutral. The diminishing of p_x by introduction the first amount of Bi_2Te_3 with the rate corresponding to the substitution Ge→Bi, shows that for small quantity of impurity, when the interaction between atoms practically is absent, the mechanism of electrical action is different. According to [17] the excess Te atoms do not destroy the anion sublattice but enter into the sublattice, partially filling the vacancies. For small concentrations of impurities, when the main contribution to the free energy is given by the entropy term, the realization of such mechanism is fully possible, because it enhances the ordering of the lattice. The increase of the impurity concentration, that leads, on one hand, to the increase of the internal energy of the crystal and, on the other hand, to the interaction of the impurity atoms, stimulates the processes related to the ordering of the structure, in particular to the formation of chemical complexes. Along the section 4 (Fig. 4.5) the most probable is the formation of the neutral components [19]. Their existence supports the constant value of p_x along the section 4 after ~1 at.% Bi.

4.2 Phase diagrams of the system SnS(Se)-Sb(Bi)

4.2.1 System SnS - Sb

The phase diagram along the section SnS-Sb has been constructed on the basis of ATD, XRD, microstructural analysis and microhardness [22] (Fig. 4.8). This section is a quasi-binary cross-section of the ternary system Sn-Sb-S. All the investigations have been carried out on homogenous samples obtained by annealing for 200 h at 620 K.

The phase diagram of the system SnS-Sb of the eutectic type, the eutectic is shifted towards the Sb side (96 mol.% Sb) and crystallizes at 888 K. The liquidus section SnS-Sb consists basically in the curve of primary crystallization of β-phase (β-solid solution based on the high temperature modification SnS). At 848 K one observes the polymorphous transition of the solid solutions based on SnS.

From microstructural analyses resulted that the solid solutions based on SnS reaches 2 mol.%. The Sb concentration introduced in SnS can be enhanced by adding Sb_2S_3. The section SnS-Sb_2S_3 is studied in [23], where are evidenced solid solutions based on both types of SnS. The boundary of the solid solution based on low temperature modification at 673 K corresponds to ~7 mol.% Sb_2Te_3.

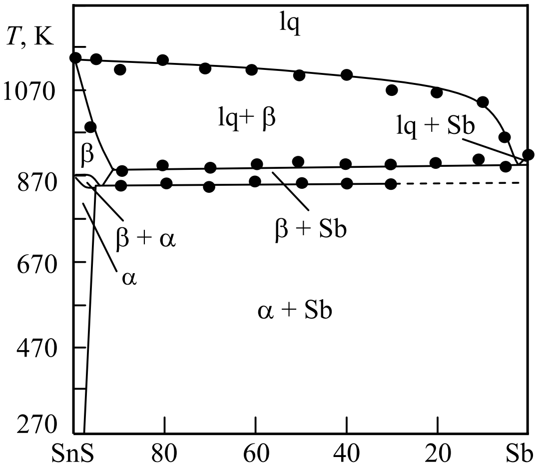

Fig. 4.8 Phase diagram of the system SnS-Sb [22].

The paper [22] reports the results of the measurements of the dependence on temperature of the electrical conductivity and coefficient of thermal electromotive force for the alloys in the domain of a solid solutions with additions: 0.5; 1.0 and 1.5 mol.% Sb in a large temperature range: 300÷800 K. It was established that all the investigations of the sample evidenced a semiconducting character of the electrical conduction and the activation energy, calculated from the domain of intrinsic conduction, decreases from 1.2 eV (for the composition with 0.5 mol.% Sb) down to 1.05 eV (for the alloy with 1.5 mol.% Sb). All the alloys from the solid solution domain based on SnS are semiconductors with p-type conductivity.

4.2.2 System SnS-Bi

The phase diagram of the system SnS-Bi and SnS-Bi_2S_3 are built on the basis of the results of microstructural analyses, ATD, microhardness and density [24]. In Fig. 4.9 are shown parts of the phase diagrams of the system SnS-Bi and SnS-Bi_2S_3 in the neighborhood of the compound SnS. In both systems are formed solid solutions based on SnS, whose boundaries, at 300 K, extend up to 3 mol.% Bi and up to 5 mol.% Bi_2S_3. By adding both bismuth and Bi_2S_3 in SnS, the polymorphous transformation of the last one in the studied diagrams shows an eutectoid character.

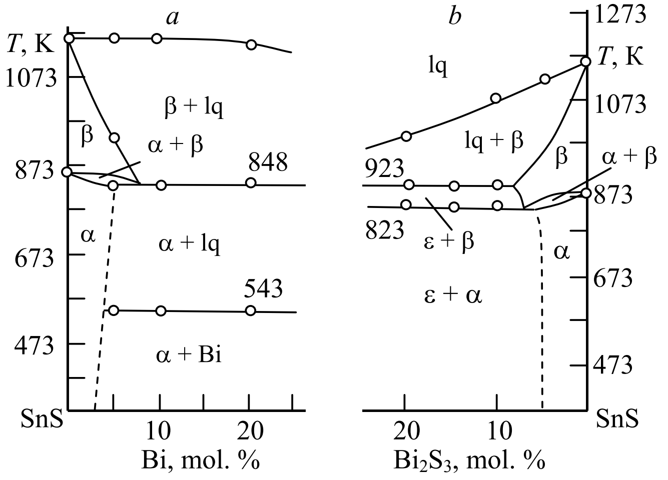

Fig. 4.9 Phase diagrams of the systems: SnS-Bi (a) and SnS-Bi_2S_3 (b) in the vicinity of the compound SnS [24].

For all the compositions of the solid solutions one observes on the curves of dependence of the conductivity on temperature, $\sigma_T = f(T)$, two domains characteristic for extrinsic and intrinsic conductivity. The substitution of Sn by bismuth in the crystalline lattice of the solid solutions is accompanied by the diminishing of the thermal width of the forbidden gap.

4.2.3 System SnSe-Sb

The phase diagram of the system SnSe-Sb was built in [25] on the basis of data of physico-chemical analyses and is represented in Fig. 4.10. The research was carried out on samples annealed at 820-840 K for 900 h. As evident from Fig. 4.10, the phase diagram of the system SnSe-Sb is quasi-binary of eutectic type. The eutectic has the composition 5 mol.% SnSe and melting temperature 873 K. There was determined the domain of solid solutions based on SnSe, which extends at room temperature up to 4 mol.% Sb. The solubility on the Sb side practically is lacking. The solid solutions $(SnS)_{1-x}Sb_x$ crystallize in rhombic singony in the structure of SnS type and the parameter of the elementary cell decreases with the increase of Sb content. On the basis of the decrease of the volume of the elementary cell with the increase of the Sb concentration in solid solutions the authors of [25] conclude that substitutional type solutions are produced.

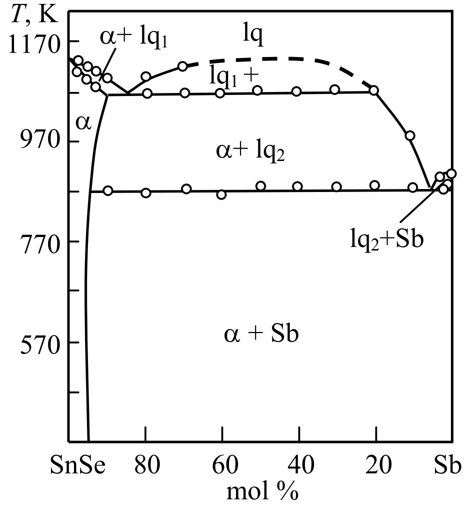

Fig. 4.10 Phase diagram of the system SnSe-Pb[25].

The thermo-electromotive force and the electrical conduction of the solid solutions $(SnSe)_{1-x}Sb_x$ sharply change when the Sb content increases. For Sb concentration x=0.5 mol.% takes place the inversion of the conductivity type from p to n and this was remarked firstly in [26]. The thermal width of the forbidden gap in the considered solid solutions decreases from 0.96 eV for pure SnSe to 0.76 eV for boundary composition of the solid solution (4 mol.% Sb).

The diagram of the condensed state of the system $SnSe$-Sb_2Se_3 is given in [27]. On the basis of low-temperature modification α-SnSe there are formed solid solutions with limited content of Sb_2Se_3: 6±1 mol.%.

4.2.4. System SnSe-Bi.

The system SnSe-Bi has been studied on annealed samples with the physico-chemical methods: X-ray diffraction, microstructural determinations and microhardness data.

The phase diagram of the system SnSe-Bi was built with the results of all investigation methods by two group of researchers [28, 29]. The resulting phase diagrams published by the two groups show differences (Fig. 4.11 a and b). According to [28] the section SnSe-Bi is a quasi-binary composition of the ternary system Sn-Se-Bi. The liquidus section SnSe-Bi consists of four branches (Fig. 4.11 a). Part of the liquidus in the concentration interval 0 ÷ 1.5 at.% Bi corresponds to primary separation of a-solid solutions on the basis of SnSe. In the concentration interval 15 ÷65 at.% and at 1073 K takes place a monotectic process. The crystallization of the alloys of composition 0 ÷ 95 at.% Bi is finished at the eutectic temperature of 533 K. Below the solid line the alloys are mixtures of the phases α-solid solutions and bismuth. The composition of the eutectic corresponds to 5 mol.% SnSe.

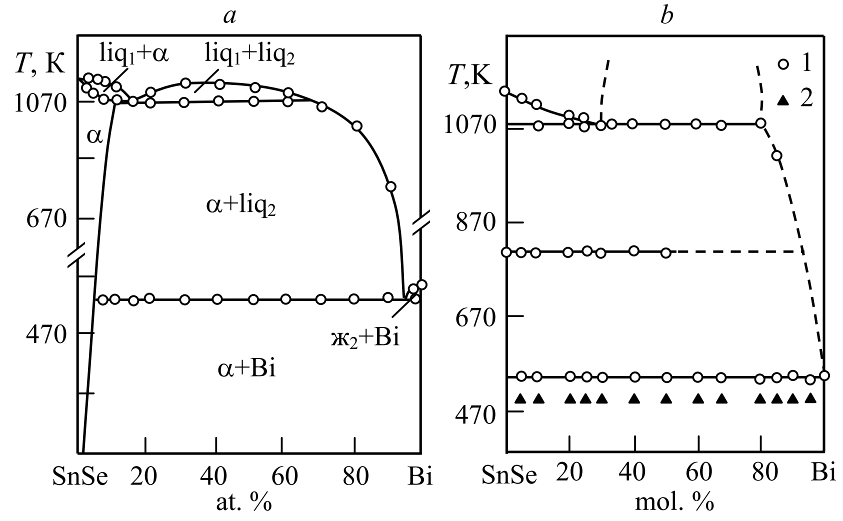

Fig. 4.11 The phase diagrams of the system SnSe-Bi: a –[28], b –[29]. 1 – data from heating curves; 2 – two-phase samples

The phase diagram of the system SnSe-Bi built in [29] is shown in Fig. 4.11. b. In the system takes place the monotectic reaction at 1078 K. In the system was observed the stratification phenomenon [28]both by microstructural investigation of the quenched samples and by XRD analysis of the solidified layers. The eutectic point of the system is sharply shifted on the Bi side. The eutectic temperature is 538 K. Not too large effects at 808 K correspond to polymorphous transformation of SnSe. All the alloys that have 1 ÷99 mol.% SnSe are two-phases and contain SnSe and Bi. The parameters of the elementary cells of the solid solutions based on $(SnSe)_{1-x}Bi_x$ remain practically constants.

In SnSe it is possible to introduce significantly higher Bi impurity amount if it is introduced BiSe and not elementary Bi. In this case the interval of solid solutions $(SnSe)_{1-x}(BiSe)_x$ extends up to 4 mol.% BiSe [29]. The dissolution of Bi_2Se_3 in β-SnSe reaches 35±3 mol.% at 943 K and sharply decreases with the decrease of the temperature. The limit of solubility of Bi_2Se_3 in α-SnSe is 12±2 mol.% at 723 K [30].

4.3 Solubility of the impurities in SnTe

The tin mono-telluride is a phase of variable composition with the homogeneity domain shifted on the side of excess tellurium. The deviation from stoichiometry determines the high concentration of the intrinsic defects of the lattice (mainly, vacancies) [12] and, correspondingly, high concentration of charge carriers of the p-type (~ 10^{20} – 10^{21} cm^{-3}). By doping of the binary non-stoichiometric semiconducting compounds with ternary alloys are determined not only the intrinsic and impurity defects, but also the interaction between them.

The analysis of the results of the study of non-stoichiometric tin mono-telluride, doped by various elements [31-35], shows that the magnitude of their limited solubility S_{lim} is essentially different. In the papers [31, 32] there were used as impurities elements of the group III (In,Ga), group IV (Pb, Sn and Ge) and group V (Sb, Bi) of the Periodic Table. The impurities have been introduced in the material with the composition $Sn_{0.984}Te$ that corresponds to the maximum on the liquidus curve in the system Sn-Te, and the crystalline lattice contained (as a consequence of deviation from stoichiometry) ~1.6 at. % of the empty cation sites. There were carried out microstructural and XRD investigations, microhardness measurements, measurements of the coefficients of the electromotive force, electrical conductivity, Hall coefficient, mobility, general thermal conductivity and calculated lattice thermal conductivity, on synthesized and annealed samples at 870 K for 300 h.

The experimental results related to the dependence on concentration of the properties of the impurities of the group IV are represented in Fig. 4.12. The transition in the hetero-phase domain is fixed enough distinctly by fractures or folds on the curves of properties as a function of concentration and also the start of the separation of particles of the second phase. The boundary of the solubility limit is shown by a dashed line. By introduction of the elements from group IV is observed the decrease of microhardness and a. From Fig. 4.12 follows that solubility of Ge and Pb does not overcome ~0.2 at.%, and solubility of Sb is much higher: ~ 0.7 at.%. A complex research of the dependence on concentration of the thermoelectrical parameters (α, σ, ae, R_x and μ) has been conducted for $Sn_{0.984}Te$, doped by lead. Introduction of Pb in tin telluride leads to the decrease of α and σ, accompanied by the increase of R_x, μ and ae_{latt} (Fig. 4.13).

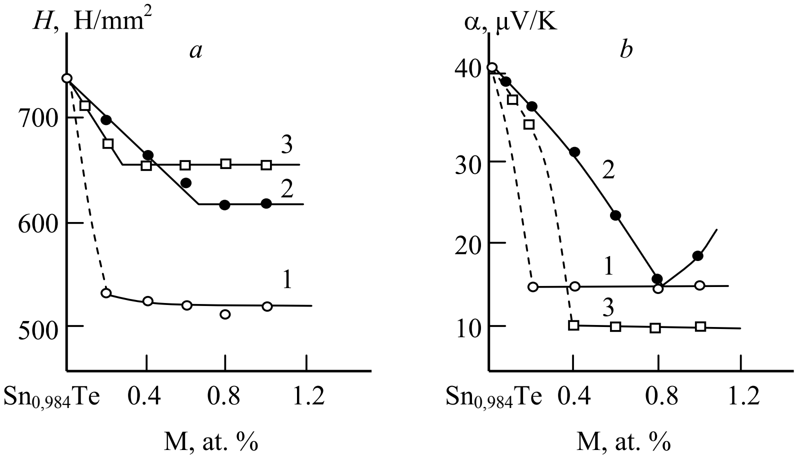

Fig. 4.12. The dependence on impurity concentrationon (M) of microhardness (H) and coefficient of the thermo-electromotive force (b) of the tin monotelluride: 1 – Pb, 2 – Sn, 3 – Ge [31].

During introduction of isoelectron impurity of the group IV in the amount comparable with the concentration of the intrinsic defects, the most probable is the localization of the impurity atoms in the cation vacancies. More larger is the crystallochemical radius of the impurity atom (ion radii

Pb^{2+},Sn^{2+}, Ge^{2+} are 1.22, 1.02 and 0.69 Å, respectively[36], more efficiently this atom compensates the deformations, related to vacancies, and more rapidly decreases H during doping. The limit of solubility of the impurity is determined by the difference of the ion radii of the basical cation (Sn) and impurity atom. For Pb, Sn Ge this difference is +20.0 and -30 %, respectively [31] and correlates well with the values of the solubility limit (0.2; 0.8 and 0.2 at.%, respectively).

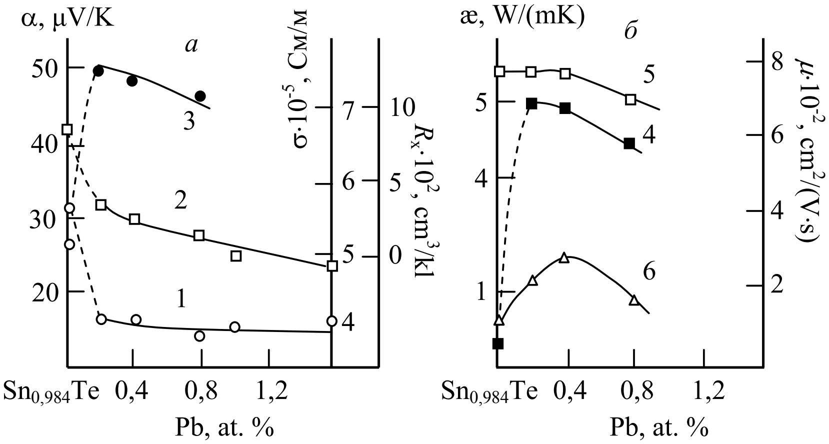

Fig. 4.13. The dependence of the thermoelectric parameters of the tin mono-telluride, doped by Pb, on the Pb concentration: 1- α, 2 - σ, 3 - R_x, 4 – μ, 5 – ae_{gen}6 – ae_{latt} [31].

The isoelectron atoms of the impurity, localized in vacancies, give their valence electrons to Te, thus diminishing the general hole concentration, and leading to the growth of R_x, and decrease of α and σ. The elimination of the distortions of the crystalline lattice by filling the vacancies determines the decrease of the scattering of phonons and electrons, and consequently, the growth of the thermo-conduction lattice component and of mobility.

The behaviour of the indium impurity in SnTe has been studied in the papers [32-40]. The investigation of the domain of solid solutions along the sections SnTe-InTe and SnTe-In_2Te_3 has been performed in [37]. From the change of the lattice parameter it has been established the homogeneity domain based on SnTe at the annealing temperature 843 K; in SnTe dissolves ~30 mol.% InTe and ~3 mol.% In_2Te_3. The dissolution isotherm of indium in tin telluride [39] is shown in Fig. 4.14. The orientation of the homogeneity domain of SnTe is situated in the direction of InTe with some deviation on the Te side, i.e. during substitution Sn →In the phase based on SnTe remains on the one-side. Consequently, the basical type of intrinsic defects in SnTe, doped by indium, and, also, in undoped SnTe, is the cation vacancy.

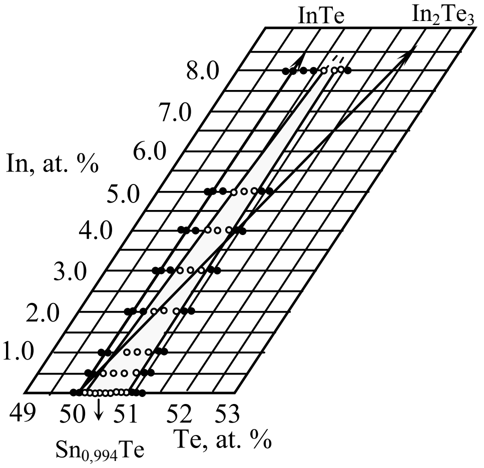

Fig. 4.14 Dissolution isotherm (823 K) in the system Sn-In-Te [39].

In the Sn-Te-In alloy indium exhibits variable valence, and the relative quantity of the indium atoms, that are in different charge states, are functions both on the concentration of the impurity atoms and on the degree of deviation from stoichiometry of the doped SnTe. The analysis of the dependence of microhardness, concentration of the charged carriers (p) and coefficient of thermo-electromotive force (α) on the indium content for fixed deviation from stoichiometry (Fig. 4.15) allows to separate in the limits of the homogeneity domain SnTe three subdomains: 1) up to ~ (0.5 ÷ 1) at.% In, microhardness practically does not change, p increases; 2) in the next composition domain, up to the crossing of the corresponding isoconcentratation line of Te with the section SnTe-In_2Te_3 microhardness, H and a increases, p decreases; in this case every introduced indium atom diminishes p with 1, playing the role of donor; 3) further a decreases, p increases, and every indium atom gives a hole. Thus, the crossing of the Te isoconcentrate line with the section SnTe-In_2Te_3 is accompanied by the change of the electrical behaviour of indium from donor to acceptor one, and, as a result, on the diagrams composition-property (α and p) of the mentioned section corresponds to the foldings with positive (α) and negative (p) curvature, respectively. Along the sections SnTe-In_2Te_3 and $Sn_{0.984}Te$-In_2Te_3 in the limits of small indium concentrations (>~1 at.%) p and a practically do not change, i.e. In_2Te_3 is a neutral addition, and InTe introduced in the stoichiometric SnTe, is an impurity of the acceptor type [39]. From the given results it follows that the section SnTe-In_2Te_3 defines domains, where the valence exhibited by indium during substitution Sn→In, and the charge state determined by such substitution (In^{1+} and In^{3+}) are different.

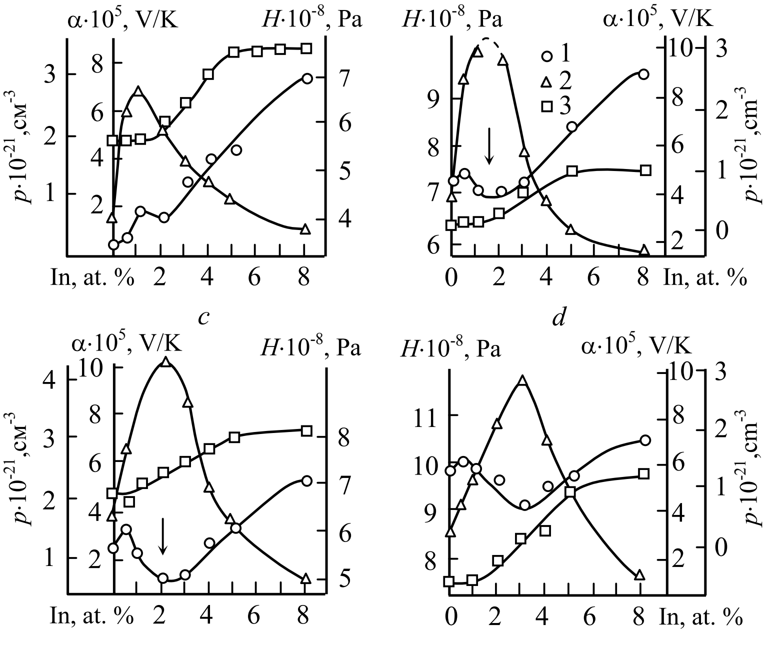

Fig. 4.15 The dependence of the concentration of the charge carriers (1), of the coefficient a of the thermo-electromotive force (2) and of microhardness (3) on the indium content along the Te isoconcentration line: a – 50.2; b – 50.6; c – 50.6; d – 50.8 at.% Te [39].

Firstly, the state diagram of the system SnTe-Sb has been built in [41] from the thermal and microstructural analyses. The section SnTe-Sb is a quasi-binary section of the eutectic type with limited solubility of the components one into another. The eutectic corresponds to the composition 15 mol.% SnTe and temperature 850 K. At 823 K the solubility of Sb in SnTe is situated in the range 1 ÷3 mol.%. Further researches of the solid solutions based on SnTe in the system Sn-Sb-Te are reported in [42-45].

The dissolution isotherm of Sb in the tin mono-telluride is represented in Fig. 4.16. The introduction of Sb leads to the shift to left and right of the boundary of the homogeneity domain of

SnTe on the side of the increase of the Te content. As a result the the homogeneity domain of SnTe is oriented along the section $Sn_{0.984}Te$-Sb_2Te_3; the solubility limit of Sb is ~9 at.% [42]. After the data reported in [43], the solubility of Sb in SnTe reaches ~10 mol.% at 823 K. In the paper [46] there were investigated the Mössbauer emission spectra at 78 K of ^{119}Sn for SnTe samples, obtained from melt, where it was introduced the radioactive marker ^{119}Sb. There was found that the Sb impurity atoms, during the formation from melt of the SnTe crystalline lattice can occupy both Sn and Te sites, and the ratio between the number of atoms in these positions strongly depends on the stoichiometry of the samples.

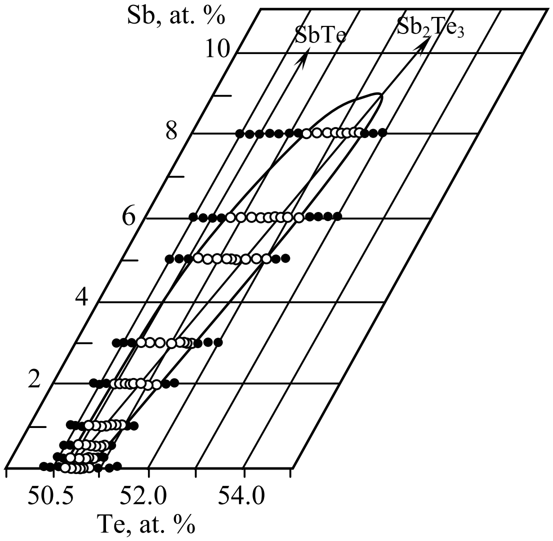

Fig. 4.16 The solubility isotherm (823 K) in the system Sn-Sb-Te[42].

The XRD investigations of the solid solutions on the basis of SnTe in the system Sn-Sb-Te have shown [46] [355], that both the increase of the Te content as well as the increase of the Sb content for constant Te concentration leads to the increase of the probability of formation of molecular complex Sb_2Te_3 and, for compositions, corresponding to the section $Sn_{0.984}Te$-Sb_2Te_3, practically all Sb atoms are linked in Sb_2Te_3 complexes, and the amount of vacancies in the matrix corresponds to the equilibrium concentration of vacancies in Sn-Te. After the intersection of the isoconcentration line of the given section new complexes do not form and the vacancies introduced increase the defects of the matrix Thus, in the solid solutions based on SnTe of the system Sn-Sb-Te takes place the chemical interaction between Sb atoms and the matrix atoms with the formation of complexes of the type Sb_2Te_3.

In solid solutions based on SnTe of the Sn-Sb-Te exhibits a non-monotonous character in the dependence of the microhardness, Hall concentration of charge carriers, and coefficient of thermo-electromotive force on the Te content along the iso-concentration line of Sb [41]. The corresponding special points of the section $Sn_{0.984}Te$-Sb_2Te_3, but not SnTe – Sb_2Te_3, show that not all vacancies in the solid solutions are linked to the complexes Sb_2Te_3: the quantity of electrically active vacancies, not bounded in the vacancies, correspond to the “equilibrium” vacancy concentration in the system Sn-Te, i.e. to concentration, which corresponds to the maximum of the melting temperature in the system Sn-Te.

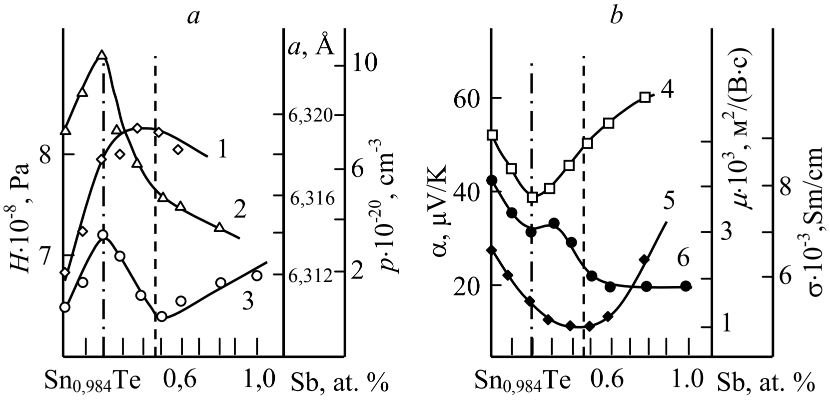

Fig. 4.17 The dependence of the parameter of the elementary cell, of the microhardness, of the charge carrier concnration (a) and the thermoelectric parameters of the tin mono-telluride (b) on the Sb content (1 – a, 2 – p, 3 – H, 4– μ, 5 – σ, 6 – α; dashed: boundary of the homogeneity domain)[32].

By introduction of In, Ga and Sb in $Sn_{0.984}Te$ the properties dependent on concentration in the limit of the solid solution domain exhibit a non-monotonous character (Fig. 4.17 and 4.18). In the interval of small concentration of impurity (up to 0.1 – 0.2 at.%) H, a and p grow (during introduction of Ga the microhardness practically remains unchanged), μ, ae_{tot} and $ae_{latt.}$ decrease. Above the limits of the above shown composition domain one observes the decrease of H and p, the increase of a is slower, $ae_{latt.}$ and u increase during introduction of Ga and Sb and not-significantly decrease by introducing indium. As a result, on the curves of dependence of p and H on concentration, during introduction of In and Sb as well as on the curves of dependence of p on concentration during introduction of Ga one observes maxima which corresponds to fractures on the curves of dependence of a, σ, α, μ and $ae_{latt.}$ on concentration. The extremal character of the curves p versus concentration indicates the change of the electrical behaviour of the impurity by increasing its concentration. The In, Ga and Sb atoms introduced in low concentrations determines the increase of p, playing the role of the acceptor impurity. The next increase of the impurity concentration leads to the change of the acceptor state in donor state. In this case, as evident, the acceptor state is accompanied by sharp deformation of the crystalline lattice, by reducing μ and $ae_{latt.}$[32].

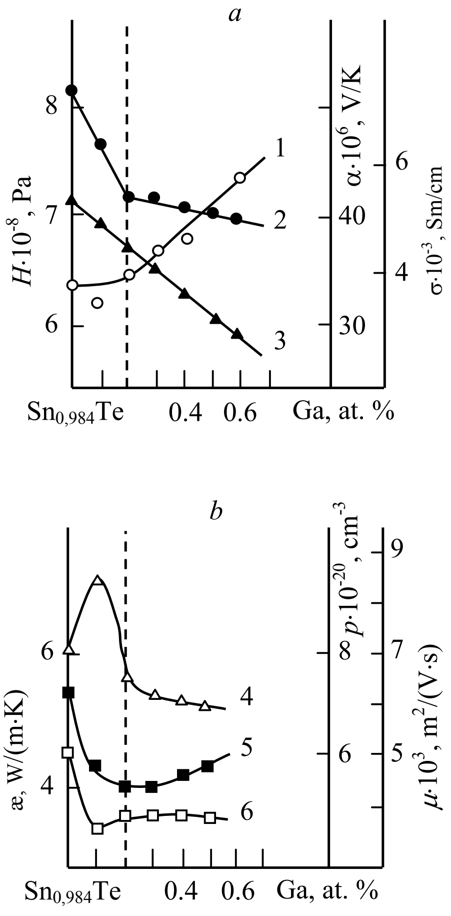

Fig. 4.18 The dependence of the microhardness and thermo-electrical parameters of the tin mono-telluride on the Ga content (a: 1 – H, 2 – σ, 3 – a; b: 4 – p, 5 – ae_{tot}, 6 – μ; dashed – boundary of the homogeneity domain)[42].

During the introduction of Bi all the properties smoothly change within the limits of the homogeneity domain: the growth of a and μ corresponds to the decrease of p, s, a, and $ae_{latt.}$ (Fig. 4.19). The non-monotonous character of the modification of both structural and thermo-electric characteristic with composition within the limit of the homogeneity domain indicates the change of the mechanism of dissolution of the impurity. The sharp increase of H and a, observed for small additions of In and Sb, speak in favour of a significant deformations of the crystalline lattice, and decrease of u and $ae_{latt.}$ – of increase of the scattering of the charge carriers and phonons on the impurity ions. Based on these facts the authors of [42] supposes that the first part of the dopant atoms enters into the crystalline lattice of SnTe by the mechanism of introduction with localization in the interstices of the cation sublattice – the tetrahedral voids of the close packing of Te atoms. Such mechanism explains the significant deformation of the crystalline lattice, the appearance of deformations, that are sources of additional scattering of electrons and phonons. By introduction of the first part of Ga the formation of the solid solutions takes place, also, as an introduction type, but due to the small size of Ga ions this does not require the significant distortions of the lattice, and H does not grow, although takes place a significant decrease of u and $ae_{latt.}$.

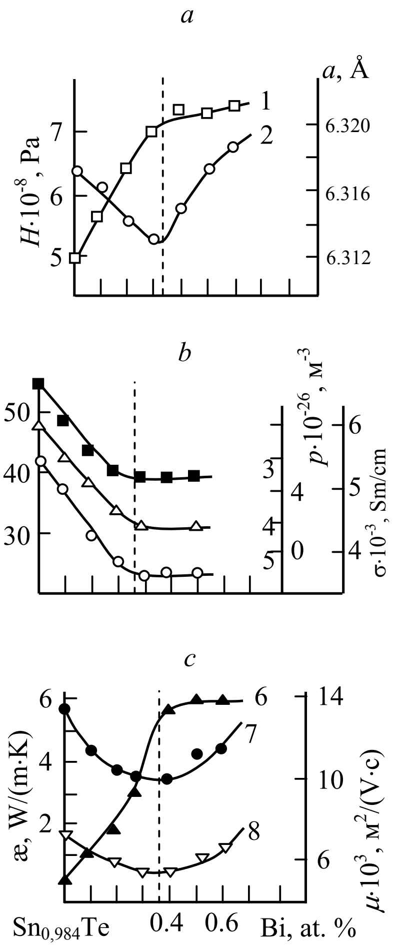

Fig. 4.19 The dependence of the parameter of the elementary cell, microhardness, charge carrier concentration (a) and thermo-electrical parameters of the tin mono-telluride (b, c) on the Bi content (1 – a, 2 - H, 3 – s, 4 – p, 5 – a, 6 –μ, 7 – ae_{tot}, 8 – $ae_{latt.}$; dashed - the boundary of the homogeneity domain). [42].

The character of the modification of the properties in the domain of impurity content higher than 0.1 – 0.2 at.% for In, Ga and Sb and in all the concentration domain for Bi indicates that the fundamental mechanism of impurity dissolution is the filling of the cation vacancies [42]. By localization of the impurity atoms in vacancies, together with the decrease of the vacancy concentration, it is enhanced the concentration of the point defects of new type: impurity defects of substitution. The observed decrease of microhardness show shows that the general level of strains in the lattice, not-considering the appearance of the new type defects, decreases. The vacancies determines the appearance of the stretching (extension) deformations near to the defects; by introduction of the impurity atom, whose size overcomes of the the vacancy size, these deformations are partially eliminated even if the cation size is smaller than the size of the tin atom. For the dimension of the cation that overcomes the size of the tin atom (case: Bi), does appear compression deformations, that partially compensate the extension deformation near to other vacancies, and H is reduced more effectively.

By filling the cation vacancies all the impurities (In, Ga, Bi, Sb) in the $Sn_{0.984}Te$ diminish p, being donors; the number of charge carriers, for every atom is in average 3 [42].

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