

UDC 535.3, 535.51

PACS numbers: 68.37.Hk, 78.66.Hf, 81.15.Ef

doi: 10.15330/jpnu.1.1.55-63

CRYSTAL-QUASICHEMICAL ANALYSIS OF DEFECT SUBSYSTEM OF DOPED PbTe: Sb CRYSTALS AND Pb-Sb-Te SOLID SOLUTIONS

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Abstract: Within crystalquasichemical formalism models of point defects of crystals in the Pb-Sb-Te system were specified. Based on proposed crystalquasichemical formulae of antimony doped crystals PbTe:Sb amphoteric dopant effect was explained. Mechanisms of solid solution formation for PbTe-Sb₂Te₃: replacement of antimony ions lead sites Sb_{Pb}^{+} with the formation of cation vacancies V_{Pb}^{2-} (I) or neutral interstitial tellurium atoms Te_i^0 (II) were examined. Dominant point defects in doped crystals PbTe:Sb and PbTe-Sb₂Te₃ solid solutions based on p-PbTe were defined. Dependences of concentration of dominant point defects, current carriers and Hall concentration on content of dopant compound and the initial deviation from stoichiometry in the basic matrix were calculated.

Keywords: lead telluride, antimony, dopant, solid solution, point defects, crystalquasichemical formulae.

1. INTRODUCTION

IV-VI compounds and solid solutions on basis of them are basic materials for making thermoelectric energy converters in high temperature region (500-750) K, as well photodetectors and radiating structures of infrared optical spectrum [1].

Among them, lead telluride has an important place due to its properties: multivalley nature of its energy spectrum ($N = 4$), low lattice thermal conductivity ($\chi = 2.09 \cdot 10^3 \text{ W} \cdot \text{K}^{-1} \text{ cm}^{-1}$), relatively high current carrier mobility ($\mu \approx 10^3 \text{ cm}^2 \text{ V}^{-1} \cdot \text{s}^{-1}$), the largest value of $\mu\chi^{-1}$, which causes a significant thermoelectric figure of merit (Z_{\max}) $Z = \alpha^2\sigma/\chi$, where α – coefficient of thermo-emf, σ – electrical conductivity, χ – coefficient of thermal conductivity. Clearly, large Z (which determined commercial use of thermoelectric material) depends on α and σ , which are sensitive to the nature of electronic states. Thermal conductivity is defined by phonon spectrum of the crystal (χ_l) and the concentration of current carriers (χ_e). Decrease of thermal conductivity components ($\chi = \chi_l + \chi_e$) is one of the effective ways of increase of the thermoelectric figure of merit. In this regard, the search for new compounds with complex crystal structures, which have low thermal conductivity is an urgent problem. Among them are quasi-binary systems ($A^{\text{IV}} - \text{Ge, Sn, Pb}$; $C^{\text{V}} - \text{Bi, Sb}$; $B^{\text{VI}} - \text{Te}$) [17].

Lead telluride crystallizes in NaCl structure, which is a characteristic of ionic crystals. Chemical bond is complex and close to the ion-covalent-metallic. PbTe is characterized by significant deviations from the stoichiometric composition and bilateral homogeneity region and can have both n-type (with

excess metal) and p-type (with excess chalcogen) conduction, causing significant concentration (10^{18} - 10^{19} cm⁻³) of electrically active intrinsic defects [7].

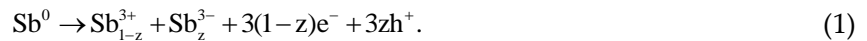
The type of PbTe-Sb diagram is eutectic. The solubility of Sb in PbTe at 820 K is 1.5 at. % [16]. Antimony, acting as a donor, moves homogeneity region limits toward higher equilibrium concentrations [14]. Solubility of Sb₂Te₃ in PbTe for PbTe-Sb₂Te₃ is defined in [9, 10, 15]. At lower temperatures (573-823) K solubility is about (2-4) at. % of Sb [9, 15]. The maximum solubility (~6 at. % Sb) obtained in the research of crystallization of PbTe-Sb₂Te₃ [8] is higher than the solubility at lower temperatures. According to [2], the boundary region of Sb₂Te₃ solubility in PbTe is approximately 2 mole %, and in [13, 15] – (4.5-5) mole %.

Performance device structures are largely determined by defect subsystem of used crystals, which depends on the homogeneity region of compounds, the chemical composition of solid solutions based on them, and technological factors of their synthesis and subsequent treatments of the material. Analyzing the current state of the problem, it should be noted that the ambiguity of the experimental data and theoretical interpretation of the nature and type of point defects and their charge states and energy parameters in crystals based on lead telluride greatly complicates the interpretation of their physical and chemical properties. Therefore, further development of theoretical approaches to the study of the defect subsystem and explanation of existing as well as new experimental data obtained from one standpoint remains an urgent problem.

2. MATERIALS AND METHODS

2.1. DOPED CRYSTALS P-PbTe:SB

2.1.1. ANALYSIS OF DOPANT BEHAVIOR. Taking into account that the valence shell of atoms of V group elements has s^2p^3 configuration, Sb atoms can give (s^2p^0 configuration, valence +3) or accept (s^2p^6 configuration, valence -3) 3 electrons from p -state. So dopant in PbTe can be in two charge states Sb³⁺ and Sb³⁻. In doped crystals PbTe:Sb fraction of electrically active impurity atoms is significantly less than 1, and it evidences that impurity atoms are distributed between the cationic and anionic sublattices [12]. Thus, in doped crystals PbTe:Sb dopant, replacing lead in its sublattice, ionizes from state Sb⁰(s^2p^3) in the state Sb³⁺(s^2p^0) + 3e⁻ and relatively Pb²⁺ sublattice it is in a state Sb³⁺ → Sb_{Pb}¹⁺ (where it is a donor). In tellurium sublattice dopant ionizes Sb⁰(s^2p^3) → Sb³⁻(s^2p^6) + 3h⁺ and is an acceptor, while relatively Te²⁻ sublattice dopant is in state Sb³⁻ → Sb_{Te}¹⁻. The fact that the dopant can occupy lead and tellurium sites in PbTe crystal structure and disproportionation of its charge state can be described by the following reaction:

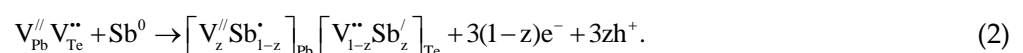


Here $z = \frac{[\text{Sb}_{\text{Te}}^{1-}]}{[\text{Sb}_{\text{Pb}}^{1+}] + [\text{Sb}_{\text{Te}}^{1-}]}$ – the value of disproportionation of dopant charge state ($0 \leq z \leq 1$), e⁻ – electrons, h⁺ – holes.

The relation between [Sb³⁺] and [Sb³⁻] determine donor or acceptor dopant effect.

2.1.2. CRYSTALQUASICHEMICAL FORMULAE. For the analysis of the defect subsystem in investigated crystals crystalquasichemical approach was used, It is based on the concept of antistructure [13], which has the form of $\mathbf{V}_{\text{Pb}}'' \mathbf{V}_{\text{Te}}^{\square}$ for lead telluride, where \mathbf{V}_{Pb}'' and $\mathbf{V}_{\text{Te}}^{\square}$ – double-charged lead and tellurium vacancies, respectively; "''" and "•" – negative and positive charges, respectively. Crystalquasichemical formula is written as a superposition of alloying cluster formed on the basis of antistructure of basic matrix and crystal formula of basic compound.

Taking into account the amphoteric effect of Sb dopant in lead telluride crystals (1), alloying cluster can be written as follows:



Crystalquasichemical formula of p-PbTe with the complex range of point defects in the cation sublattice (single and double-charged Pb vacancies) is represented as [4]:

$$\left[\text{Pb}_{1-\beta}^x \text{V}_{\beta(1-\delta)}^{//} \text{V}_{\beta\delta}^{/} \right]_{\text{Pb}} \left[\text{Te}_{1-\beta\gamma}^x \text{V}_{\beta\gamma}^{**} \right]_{\text{Te}} \left(\text{Te}_{\beta\gamma}^x \right)_i + \beta(2-2\gamma-\delta)h^+ \quad (3)$$

Superposition of crystalquasichemical formula of p-PbTe (3) and the alloying cluster (2) presents the crystal-quasichemical formula of p-PbTe:Sb:

$$\left[\text{Pb}_{(1-\beta)(1-x)}^x \text{Sb}_{(1-z)x}^{\cdot} \text{V}_{\beta(1-\delta)(1-x)+zx}^{//} \text{V}_{\beta\delta(1-x)}^{/} \right]_{\text{Pb}} \left[\text{Te}_{(1-\beta\gamma)(1-x)}^x \text{Sb}_{zx}^{/} \text{V}_{\beta\gamma(1-x)+(1-z)x}^{**} \right]_{\text{Te}} \left(\text{Te}_{\beta\gamma(1-x)}^x \right)_i + \quad (4)$$

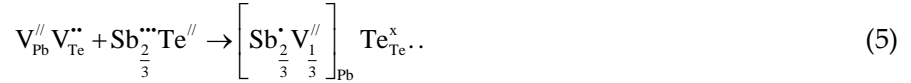
$$+ (\beta(2-2\gamma-\delta)(1-x) + 3zx)h^+ + 3(1-z)xe^-,$$

where x – atomic fraction of dopant (Sb), β – the value of the initial deviation from stoichiometry on the side of Te, δ – coefficient of disproportionation of cationic vacancies charge state, γ – fraction of interstitial tellurium, Te_i^x – interstitial tellurium, Pb_{Pb}^x , Te_{Te}^x – lead and tellurium atoms in lattice sites.

2.2. SOLID SOLUTIONS P-PbTe-Sb₂Te₃

The possible mechanisms of PbTe-Sb₂Te₃ solid solution formation are substitution of Sb ions Pb sites with the formation of cation vacancies (mechanism I) or the substitution of Sb ions Pb site with the formation of interstitial tellurium (mechanism II).

2.2.1. MECHANISM I. At calculation per 1 tellurium atom and subject to charge state of Sb³⁺ and Te²⁻ ions chemical formula for alloying component is: $\text{Sb}_{2/3}^{3+}\text{Te}^{2-}$. Alloying cluster in this case is:

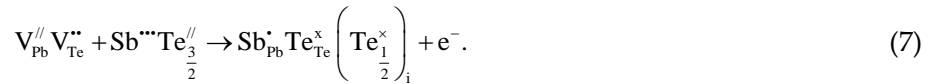


Then crystalquasichemical formula of p-PbTe-Sb₂Te₃ is:

$$\left[\text{Pb}_{(1-\beta)(1-x)}^x \text{Sb}_{\frac{2}{3}x}^{\cdot} \text{V}_{\beta(1-\delta)(1-x)+\frac{1}{3}x}^{//} \text{V}_{\beta\delta(1-x)}^{/} \right]_{\text{Pb}} \left[\text{Te}_{(1-\beta\gamma)(1-x)+x}^x \text{V}_{\beta\gamma(1-x)}^{**} \right]_{\text{Te}} \left(\text{Te}_{\beta\gamma(1-x)}^x \right)_i + \beta(2-2\gamma-\delta)(1-x)h^+, \quad (6)$$

where x – molar fraction of Sb₂Te₃.

2.2.2. MECHANISM II. At calculation per 1 Sb atom and subject to charge state of Sb³⁺ and Te²⁻ ions chemical formula for alloying components is written as: $\text{Sb}^{3+}\text{Te}_{3/2}^{2-}$, and its cluster is:



Then crystalquasichemical formula of p-PbTe-Sb₂Te₃ is:

$$\left[\text{Pb}_{(1-\beta)(1-x)}^x \text{Sb}_x^{\cdot} \text{V}_{\beta(1-\delta)(1-x)}^{//} \text{V}_{\beta\delta(1-x)}^{/} \right]_{\text{Pb}} \left[\text{Te}_{(1-\beta\gamma)(1-x)+x}^x \text{V}_{\beta\gamma(1-x)}^{**} \right]_{\text{Te}} \left(\text{Te}_{\beta\gamma(1-x)+\frac{1}{2}x}^x \right)_i + \beta(2-2\gamma-\delta)(1-x)h^+ + xe^- \quad (8)$$

2.3. ELECTRIC BALANCE EQUATION

Proposed mechanisms of doping and crystal formulae (4), (6), (8) make it possible to find analytical expressions of the concentration of individual point defects and current carriers on the magnitude of deviation from stoichiometric composition in the base compound (α , β) and dopant content (x).

In particular for p-PbTe:Sb according to crystalquasichemical formula (4), total electroneutrality equation is written as follows:

$$n + |q_{V_{Pb}''}| [V_{Pb}'''] + |q_{V_{Pb}'}| [V_{Pb}'] + |q_{Sb_{Te}'}| [Sb_{Te}'] = p + |q_{V_{Te}''}| [V_{Te}'''] + |q_{Sb_{Pb}'}| [Sb_{Pb}'], \quad (9)$$

where

$$\begin{aligned} p &= A(\beta(2-2\gamma-\delta)(1-x) + 3zx), \\ n &= 3A(1-z)x, \\ [Sb_{\alpha}'] &= Azx, \\ [V_{Pb}'] &= A\beta\delta(1-x), \\ [V_{Pb}'''] &= A(\beta(1-\delta)(1-x) + zx), \\ [Sb_{Pb}'] &= A(1-z)x, \\ [V_{Te}'''] &= A(\beta\gamma(1-x) + (1-z)x), \\ |q_{V_{Pb}'}| &= |q_{Sb_{Pb}'}| = |q_{Sb_{\alpha}'}| = 1, \\ |q_{V_{Pb}''}| &= |q_{V_{Te}''}| = 2 \end{aligned}$$

Here $A = \frac{2Z}{a^3}$, Z – number of structural units per unit cell ($Z = 4$), a – lattice parameter.

Hall concentration of current carriers n_H in this case is defined as:

$$n_H = A|3(1-z)x - \beta(2-2\gamma-\delta)(1-x) - 3zx|. \quad (10)$$

Similar analysis was done for $PbTe-Sb_2Te_3$ solid solution.

3. RESULTS AND DISCUSSION

3.1. DOPED CRYSTALS P-PbTe:Sb

In doped $PbTe:Sb$ crystals when the value of $z < 0.5$ admixture does donor action ($[Sb_{Pb}^{1+}] > [Sb_{Te}^{1-}]$): decrease of hole concentration, thermodynamic p-n-conversion and the subsequent increase of the electron concentration. With the predominance of impurity ions in tellurium sites $z > 0.5$ ($[Sb_{Pb}^{1+}] < [Sb_{Te}^{1-}]$) there is the opposite dependence: significant increase of the concentration of majority carriers. If $z = 0.5$ there is complete self-compensation of dopant ($[Sb_{Pb}^{1+}] = [Sb_{Te}^{1-}]$), and Hall concentration in both cases decreases slightly. Above-mentioned specific behavior of Hall concentration depending on the content of dopant and its charge state is well illustrated on 3d-diagram n_H - x - z (Fig. 1).

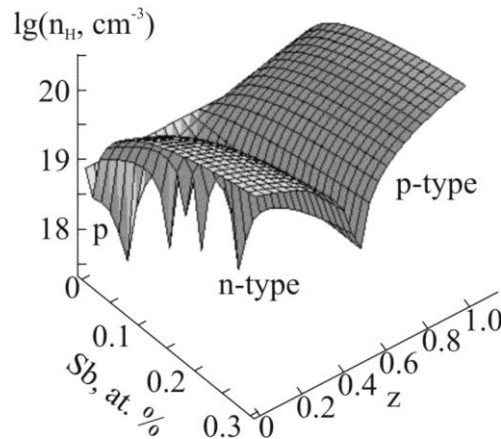


Fig. 1. Dependence of Hall concentration (n_H) in p - $PbTe:Sb$ crystals on dopant content and the value of disproportionation of its charge state (z)

Change of Hall concentration is associated with redistribution of dominant point defects concentration. Thus, dominant defects are antimony ions rooted in lead sublattice $\text{Sb}_{\text{Pb}}^{1+}$ and tellurium sublattice $\text{Sb}_{\text{Te}}^{1-}$ of lead telluride crystal lattice, which concentration increases with dopant content increase (Fig. 2 – curves 2, 3). Doubly ionized vacancies of lead [$\text{V}_{\text{Pb}}^{2-}$] and doubly charged vacancies of tellurium [$\text{V}_{\text{Te}}^{2+}$] also give significant contribution to the conductivity. Concentrations of $\text{V}_{\text{Pb}}^{2-}$ and $\text{V}_{\text{Te}}^{2+}$ increases with dopant content increase (Fig. 2 – curves 4, 6). It should be noted that the concentration of $\text{V}_{\text{Pb}}^{1-}$, Te_i^0 vary slightly with antimony content increase (Fig. 2 – curves 5, 7).

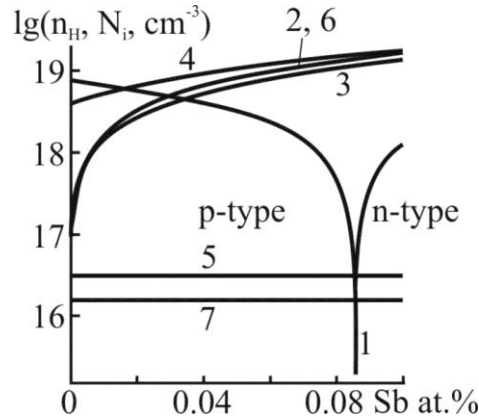


Fig. 2. Dependence of Hall concentration (1 – n_H) and the concentration of point defects (2-7 – N_i) in *p*-PbTe:Sb crystals on dopant content. N_i : 2 – $\text{Sb}_{\text{Pb}}^{1+}$; 3 – $\text{Sb}_{\text{Te}}^{1-}$; 4 – $\text{V}_{\text{Pb}}^{2-}$; 5 – $\text{V}_{\text{Pb}}^{1-}$; 6 – $\text{V}_{\text{Te}}^{2+}$; 7 – Te_i^0 ($z = 0.45$)

The proposed mechanism of doping satisfactorily explains the experimentally observed behavior of thermoelectric parameters on dopant content. Thus, based on the data of [3, 5, 11] we can conclude that, in practice, there is realization of condition: $z < 0.5$, ie the concentration of impurity ions [$\text{Sb}_{\text{Pb}}^{1+}$] overrides [$\text{Sb}_{\text{Te}}^{1-}$]. Specifically, comparing the experimental data [5] on the active donor action of antimony (Fig. 3) with the calculation for *p*-PbTe:Sb (Fig. 1), it was found the value of disproportionation of dopant charge state: $z \approx 0.45$ at the maximum value of the initial deviation from stoichiometry on the side of tellurium. The observed decrease of the concentration of current carriers in PbTe:Sb (Fig. 3 – curve 2) in the content of Sb over ~ 0.3 at. % can be explained by certain predominance of concentrations of impurity ions in tellurium sites ($[\text{Sb}_{\text{Pb}}^{1+}] < [\text{Sb}_{\text{Te}}^{1-}]$).

3.2. SOLID SOLUTIONS P-PbTe-Sb₂Te₃

Thermoelectric parameters of PbTe-Sb₂Te₃ were studied in several papers [10, 13, 15, 17, 18]. In [15] it was found that the increase of Sb₂Te₃ content in solid solution leads to donor effect with microhardness increase (H) (Fig. 4 – curve 1) and decrease of the coefficient of thermo-emf (α) (Fig. 4 – curve 3). In alloys containing Sb₂Te₃ more (1.5-2) mole % Hall concentration n_H (Fig. 4 – curve 2) and thermo-emf α (Fig. 4 – curve 3) practically do not change. Issues associated with the decrease of the value of thermal conductivity of PbTe-Sb₂Te₃ solid solutions with Sb₂Te₃ content increase were studied in [14, 18]. The value of χ for alloy of PbTe with 1.02 mole % Sb₂Te₃ is $1.25 \cdot 10^{-2} \text{ WK}^{-1}\text{cm}^{-1}$ at 500 K, which confirms the idea of the good thermoelectric efficiency of these solid solutions. The observed phenomenon associated with relation between lattice (χ_l) and electron (χ_e) components of thermal conductivity [17].

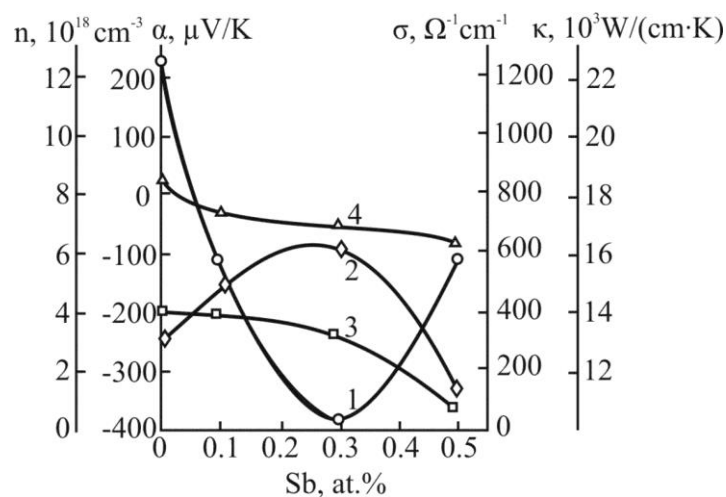


Fig. 3. Dependence of thermoelectric parameters of PbTe:Sb crystals: coefficient of thermo-emf (1 – α), current carrier concentration (2 – n), electrical conductivity (3 – σ) and thermal conductivity (4 – κ) on antimony content [5]

Consider in detail the mechanisms of defect formation in PbTe-Sb₂Te₃ solid solutions. When realization of mechanism I (stoichiometry for chalcogen) there is slight decrease of concentration of major current carriers with Sb₂Te₃ fraction increase (Fig. 5, a – curve 1). With realization of mechanism II (stoichiometry for antimony) in p-PbTe-Sb₂Te₃ (Fig. 5, b – curve 1) with Sb₂Te₃ fraction increase there is decrease of the concentration of current carriers, change of the conductivity type with low dopant content and further increase of electron concentration. Comparing the results of calculations with experimental data on the active donor effect of Sb₂Te₃ (Fig. 4 – curve 2), we can conclude that when the dopant content to 2 mole % of Sb₂Te₃ mechanism II is dominant, and with more of its contents (up to the limit of solubility) mechanism I is dominant.

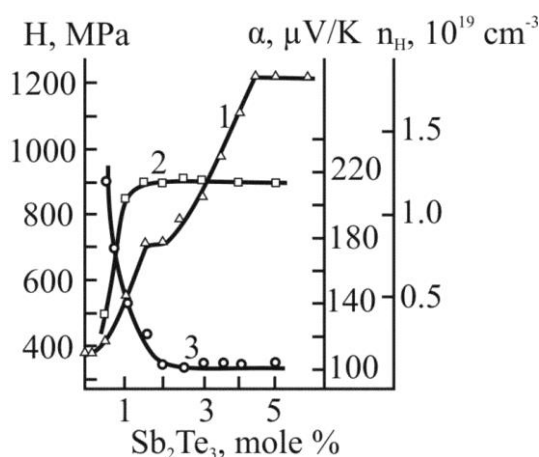


Fig. 4. Dependence of microhardness (1 – H), Hall concentration (2 – n_H) and coefficient of thermo-emf (3 – α) of PbTe-Sb₂Te₃ solid solutions on Sb₂Te₃ content [15]

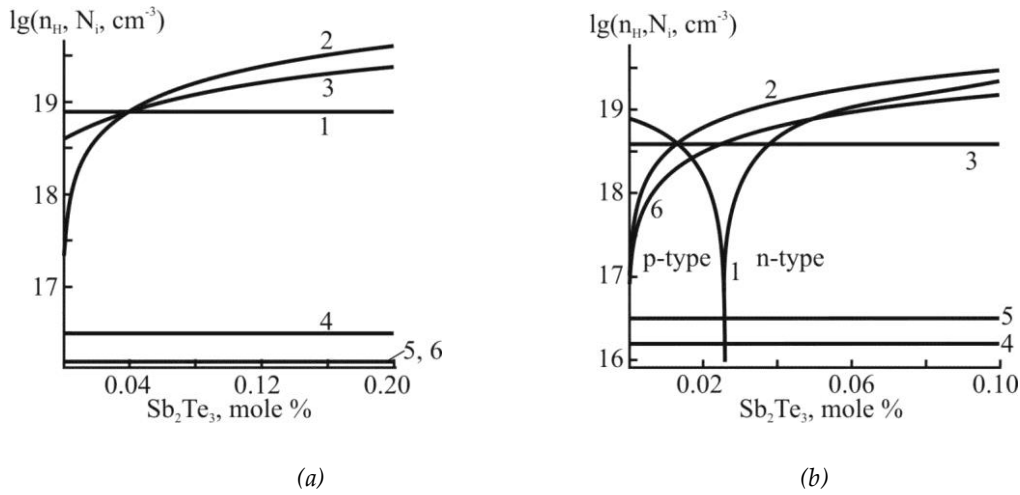


Fig. 5. Dependence of Hall concentration ($1 - n_H$) and the concentrations of point defects ($2-6 - N_i$) in p -PbTe- Sb_2Te_3 solid solutions on Sb_2Te_3 content at mechanism I (a) and mechanism II (b) realization. N_i : 2 - Sb_{Pb}^{1+} ; 3 - V_{Pb}^{2-} ; 4 - V_{Pb}^{1-} ; 5 - V_{Te}^{2+} ; 6 - Te_3^0

Features observed in the change of current carrier concentration are associated with typical correlations between individual point defects (Fig. 5). Thus, for the mechanism I in p -PbTe- Sb_2Te_3 crystals with Sb_2Te_3 content increase there is significant increase of the concentration of ionized antimony in lead sites Sb_{Pb}^{1+} (Fig. 5, a – curve 2) and doubly charged cation vacancies V_{Pb}^{2-} (Fig. 5, a – curve 3). Concentrations of V_{Pb}^{1-} , V_{Te}^{2+} , Te_3^0 decrease slightly (Fig. 5, a – curves 4, 5, 7). For mechanism II in p -PbTe- Sb_2Te_3 crystals the dominant defects are Sb_{Pb}^{1+} , Te_3^0 , V_{Pb}^{2-} (Fig. 5, b). Concentrations $[Sb_{Pb}^{1+}]$ and $[Te_3^0]$ increase with dopant content increase (Fig. 5, b – curves 2, 7), and $[V_{Pb}^{2-}]$ decreases slightly (Fig. 5, b – curve 3). Point defects V_{Pb}^{1-} and V_{Te}^{2+} do not significantly affect the conductivity. Concentration of V_{Pb}^{1-} and V_{Te}^{2+} does not change with Sb_2Te_3 content increase (Fig. 5, b – curves 4, 5). Thus, the contribution to the conductivity of substitution defects Sb_{Pb}^{1+} increases, and V_{Pb}^{2-} decreases with dopant content increase.

4. CONCLUSIONS

Based on first proposed crystalquasichemical formulae that take into account the amphoteric behavior of Sb in PbTe crystals, it has been found that with prevalence of antimony in cation sites $[Sb_{Pb}^{1+}] > [Sb_{Te}^{1-}]$, dopant is the donor, and with prevalence of Sb in anion sites ($[Sb_{Pb}^{1+}] < [Sb_{Te}^{1-}]$) dopant is the acceptor, and when $[Sb_{Pb}^{1+}] = [Sb_{Te}^{1-}]$ there is a complete self-compensation of influence of dopant.

It has been shown that in doped crystals PbTe:Sb experimental results are explained satisfactorily provided $[Sb_{Pb}^{1+}] > [Sb_{Te}^{1-}]$. Thus the dominant defects are impurity defects Sb_{Pb}^{1+} , Sb_{Te}^{1-} and vacancies of lead V_{Pb}^{2-} and tellurium V_{Te}^{2+} , which concentration increases with dopant content increase, and the ratio between them determines the type of conductivity of the material.

It has been determined that the value of disproportionation of charge state of dopant in PbTe:Sb is $z \approx 0.45$.

It has been shown that with increasing content of alloying compound in PbTe- Sb_2Te_3 solid solutions to 2 mole % of Sb_2Te_3 substitutions of cation sites and the formation of interstitial tellurium predominant. With more dopant content (up to the limit of solubility) there is a replacement of Pb sites and formation of cation vacancies. In the first case there is thermodynamic p-n-conversion in crystals with the initial p-type conductivity. For the second case there is decrease of Hall concentration in p -PbTe- Sb_2Te_3 .

It has been shown that new crystal approaches deepen the possibility of a scientific analysis of the defect subsystem in semiconductor crystals, and determine the technological aspects of the property control.

Work is implemented within the framework of state budget № 0107U006768 of Ministry of Education and Science of Ukraine.

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Received: 14.10.2013; **revised:** 10.02.2014

Фреїк Д.М., Туровська Л.В. Кристалоквазіхімічний аналіз дефектної підсистеми легованих кристалів PbTe:Sb та твердих розчинів Pb-Sb-Te. *Журнал Прикарпатського університету імені Василя Стефаника*, **1** (1) (2014), 55–63.

У рамках кристалоквазіхімічного формалізму уточнено моделі точкових дефектів у кристалах системи Pb-Sb-Te. На основі запропонованих кристалоквазіхімічних формул пояснено амфотерну дію домішки у легованих сурмою кристалах PbTe:Sb. Досліджено механізми утворення твердого розчину PbTe-Sb₂Te₃: заміщення йонами стибію позицій плюмбуму Sb_{Pb}¹⁺ з утворенням катіонних вакансій V_{Pb}²⁻ (I) або нейтральних атомів телуру в міжвузлі (II). Визначені домінуючі точкові дефекти у легованих кристалах PbTe:Sb і твердих розчинах PbTe-Sb₂Te₃ на основі р-PbTe. Розраховано залежності концентрації домінуючих точкових дефектів, носіїв заряду і холлівської концентрації від вмісту легуючої сполуки та величини початкового відхилення від стехіометрії в основній матриці. .

Ключові слова: телурид свинцю, сурми, домішка, твердий розчин, точкові дефекти, кристалоквазіхімічна формула.