ISSN: 2319-5967
ISO 9001:2008 Certified
International Journal of Engineering Science and Innovative Technology (IJESIT)
Volume 3, Issue 2, March 2014

Crystal Chemical and Thermodynamic Approaches to the Modeling of Defect Subsystem of Nonstoichiometric Lead Telluride

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Abstract* — *Quasi chemical and crystal quasi chemical formulae of defect subsystem of nonstoichiometric PbTe crystals were offered. Values of equilibrium constants of quasi chemical reactions of point defects generation in lead telluride were specified. Using the method based on minimizing of thermodynamic potentials of "crystal-vapour" system, equilibrium concentration of point defects and current carriers depending on technological factors of two-temperature annealing were calculated. The homogeneity region boundaries of PbTe were specified.

Index Terms **— crystal quasi chemistry, equilibrium constants, homogeneity region, lead telluride, point defects, quasi chemistry, thermodynamic potential, two-temperature annealing.**

I. 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 photo detectors 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, relatively high current carrier mobility, which causes a significant thermoelectric figure of merit. 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 [2].

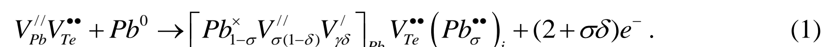
Performance device structures are largely determined by defect subsystem of used crystals, which depends on the homogeneity region of compounds, the chemical composition of solid solutions based on them, and technological factors of their synthesis and subsequent treatments of the material. Analyzing 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.

II. RESULTS AND DISCUSSION

A. *Crystal quasi chemical Approache*

The method of crystal quasi chemical analysis of defect subsystem is based on the notion of antistructure on the basis of which the superposition crystal quasi chemical clusters of basic and doping compounds [3]. Antistructure of lead telluride is $V_{Pb}^{//}V_{Te}^{\bullet\bullet}$, where $V_{Pb}^{//}$ and $V_{Te}^{\bullet\bullet}$ – doubly negatively charged vacancy of lead and doubly positively charged vacancy of tellurium, „$^{/}$" and „$^{\bullet}$" – negative and positive charges, respectively.

Crystal quasi chemical cluster of n-PbTe (excess lead in the range of the homogeneity region) subject to disproportionation of vacancies in the cation sub lattice:



$$V_{Pb}^{//}V_{Te}^{\bullet\bullet} + Pb^{0} \rightarrow \left[Pb_{1-\sigma}^{\times}V_{\sigma(1-\delta)}^{//}V_{\gamma\delta}^{/}\right]_{Pb} V_{Te}^{\bullet\bullet}\left(Pb_{\sigma}^{\bullet\bullet}\right)_{i} + (2+\sigma\delta)e^{-} . \quad (1)$$

And crystal quasi chemical formula of n-PbTe is:

ISSN: 2319-5967

ISO 9001:2008 Certified

International Journal of Engineering Science and Innovative Technology (IJESIT)

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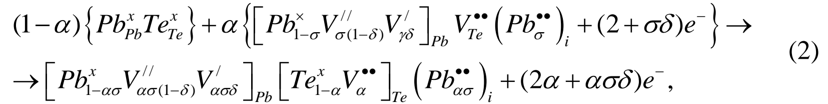
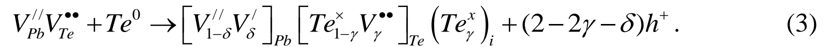


$$(1-\alpha)\left\{Pb^{x}_{Pb}Te^{x}_{Te}\right\}+\alpha\left\{\left[Pb^{x}_{1-\sigma}V^{//}_{\sigma(1-\delta)}V^{/}_{\gamma\delta}\right]_{Pb}V^{\bullet\bullet}_{Te}\left(Pb^{\bullet\bullet}_{\sigma}\right)_i+(2+\sigma\delta)e^{-}\right\}\to$$
$$\to\left[Pb^{x}_{1-\alpha\sigma}V^{//}_{\alpha\sigma(1-\delta)}V^{/}_{\alpha\sigma\delta}\right]_{Pb}\left[Te^{x}_{1-\alpha}V^{\bullet\bullet}_{\alpha}\right]_{Te}\left(Pb^{\bullet\bullet}_{\alpha\sigma}\right)_i+(2\alpha+\alpha\sigma\delta)e^{-}, \quad (2)$$

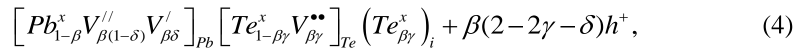
where $Pb^{\times}_{Pb}$, $Te^{\times}_{Te}$ – lead and tellurium in lattice sites of PbTe, α – deviation from stoichiometry on the side of Pb, δ – coefficient of disproportionation of charge state of lead vacancies, "x" – neutral charge, σ – share of interstitial lead, e^{-} – electrons.

Similarly crystal quasi chemical representation of non stoichiometric *p*-PbTe (excess tellurium in the range of the homogeneity region) is described as:



$$V^{//}_{Pb}V^{\bullet\bullet}_{Te}+Te^{0}\to\left[V^{//}_{1-\delta}V^{/}_{\delta}\right]_{Pb}\left[Te^{\times}_{1-\gamma}V^{\bullet\bullet}_{\gamma}\right]_{Te}\left(Te^{x}_{\gamma}\right)_i+(2-2\gamma-\delta)h^{+}. \quad (3)$$

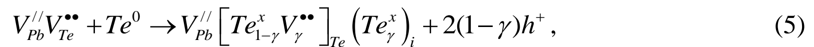
Crystal quasi chemical formula of *p*-PbTe is:



$$\left[Pb^{x}_{1-\beta}V^{//}_{\beta(1-\delta)}V^{/}_{\beta\delta}\right]_{Pb}\left[Te^{x}_{1-\beta\gamma}V^{\bullet\bullet}_{\beta\gamma}\right]_{Te}\left(Te^{x}_{\beta\gamma}\right)_i+\beta(2-2\gamma-\delta)h^{+}, \quad (4)$$

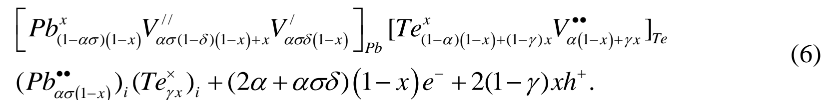
where β – magnitude of initial deviation from stoichiometry on the side of Te, γ – share of interstitial tellurium, h^{+} – holes.

Consider the process of self-doping of lead telluride. For *n*-PbTe process of self-doping by tellurium are described follows. Alloying cluster is:



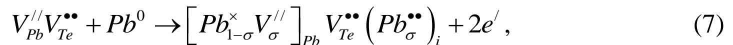
$$V^{//}_{Pb}V^{\bullet\bullet}_{Te}+Te^{0}\to V^{//}_{Pb}\left[Te^{x}_{1-\gamma}V^{\bullet\bullet}_{\gamma}\right]_{Te}\left(Te^{x}_{\gamma}\right)_i+2(1-\gamma)h^{+}, \quad (5)$$

and crystal quasi chemical formula of *n*-PbTe:Te:



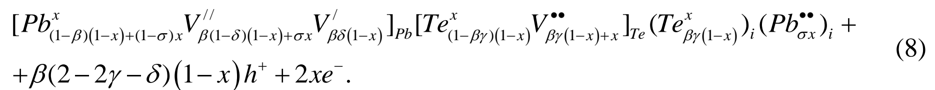
$$\left[Pb^{x}_{(1-\alpha\sigma)(1-x)}V^{//}_{\alpha\sigma(1-\delta)(1-x)+x}V^{/}_{\alpha\sigma\delta(1-x)}\right]_{Pb}[Te^{x}_{(1-\alpha)(1-x)+(1-\gamma)x}V^{\bullet\bullet}_{\alpha(1-x)+\gamma x}]_{Te}$$
$$(Pb^{\bullet\bullet}_{\alpha\sigma(1-x)})_i(Te^{\times}_{\gamma x})_i+(2\alpha+\alpha\sigma\delta)(1-x)e^{-}+2(1-\gamma)xh^{+}. \quad (6)$$

For the case of lead telluride with predominant p-type conductivity doped by lead alloying cluster is:



$$V^{//}_{Pb}V^{\bullet\bullet}_{Te}+Pb^{0}\to\left[Pb^{\times}_{1-\sigma}V^{//}_{\sigma}\right]_{Pb}V^{\bullet\bullet}_{Te}\left(Pb^{\bullet\bullet}_{\sigma}\right)_i+2e^{/}, \quad (7)$$

and crystal quasi chemical formula of *p*-PbTe:Pb is:



$$[Pb^{x}_{(1-\beta)(1-x)+(1-\sigma)x}V^{//}_{\beta(1-\delta)(1-x)+\sigma x}V^{/}_{\beta\delta(1-x)}]_{Pb}[Te^{x}_{(1-\beta\gamma)(1-x)}V^{\bullet\bullet}_{\beta\gamma(1-x)+x}]_{Te}(Te^{x}_{\beta\gamma(1-x)})_i(Pb^{\bullet\bullet}_{\sigma x})_i+$$
$$+\beta(2-2\gamma-\delta)(1-x)h^{+}+2xe^{-}. \quad (8)$$

Obtained crystal quasi chemical formulae (2)-(8) make it possible to calculate the concentration of point defects and current carriers (*n*, *p*) in *n*-PbTe:Te and *p*-PbTe:Pb crystals. In the case of self-doping of *n*-PbTe by tellurium the concentration of electrons decreases, the conductivity type changes and the concentration of holes increases (Figure 1, a). The opposite situation is observed in *p*-PbTe self-doped by lead (Figure 1, b): decrease of the concentration of major carriers, changing the conductivity type, the growth of the electron concentration.

The observed behaviour of the Hall concentration is associated with a change in the ratio of point defects. In the case of *n*-PbTe:Te (Figure 1, a) doubly charged vacancies of lead V^{2-}_{Pb} and tellurium V^{2+}_{Te} give greatest contribution to the conductivity (Figure 1, a – curves 2, 3). The concentration of V^{2-}_{Pb} increases significantly (Figure 1, a – curve 2). The change of the ratio of cation and anion vacancies has greatest effect on the variation of conductivity type of self-doped lead telluride crystals. The concentrations of point defects Pb^{2+}_{i}, Te^{0}_{i} and V^{1-}_{Pb} are significantly smaller (Figure 1, a – curves 4, 5, 6); the concentration of interstitial tellurium Te^{0}_{i} increases with the content of superstoichiometric tellurium (Figure 1, a – curve 5).

In the case of *p*-PbTe:Pb (Figure 1, b) vacancies of lead V^{2-}_{Pb} and tellurium V^{2+}_{Te} give greatest contribution to the conductivity (Figure 1, b – curves 2, 3), the concentration of V^{2+}_{Te} increases with the dopant content (Figure 1, b – curve 3). Concentrations of Te^{0}_{i} and V^{1-}_{Pb} are much smaller (Figure 1, b – curves 5, 6) and virtually no change; concentration of interstitial lead Pb^{2+}_{i} is negligible and increases with the content of the alloying component (Figure 1, b – curve 4).

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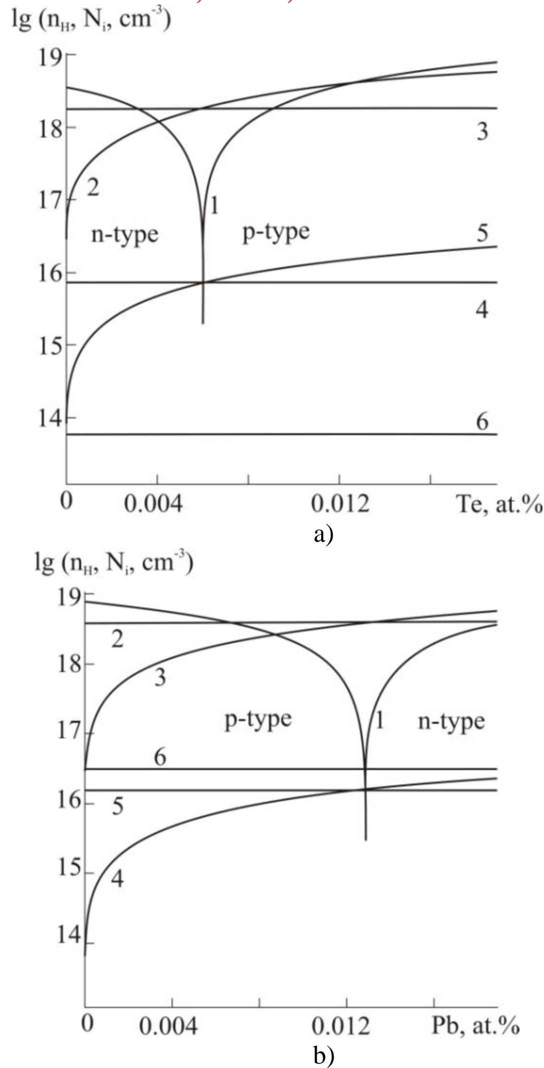

Fig 1. Dependences of Hall concentration of current carriers (1 – n_H), the concentration of point defects N_i (2 – V_{Pb}^{2-}, 3 – V_{Te}^{2+}, 4 – Pb_i^{2+}, 5 – Te_i^0, 6 – V_{Pb}^{1-}) in self-doped crystals: *n*-PbTe:Te (a) and *p*-PbTe:Pb (b) on the dopant content (at.%: δ = 0,8, γ = 0,4, σ = 0,4)

B. Quasi chemical Approache

Stoichiometric composition of lead telluride can be changed by setting the partial pressure of the components (lead, tellurium) on the solid phase or the temperature in the method of two-temperature annealing.
Equilibrium of "crystal-vapour" in this case can be described by combined equations of quasi chemical reactions listed in Table 1.

Table 1: Quasi chemical reactions of point defects at two-temperature annealing

№	Equation of reaction	Equilibrium constant	K^0, (cm^{-3}, Pa)	ΔH, eV
I	$"0" = V_{Pb}^0 + V_{Te}^0$	$K_S = \left[V_{Pb}^0\right]\cdot\left[V_{Te}^0\right]$	4,8·10^{48}	2,96
II	$\frac{1}{2}Te_2^V = V_{Pb}^0 + Te_{Te}^0$	$K_{Te_2V} = \left[V_{Pb}^0\right]\cdot P_{Te_2}^{-1/2}$	2,5·10^{18}	0,28
III	$V_{Te}^0 = V_{Te}^{2+} + 2e^-$	$K_a^{/} = \left[V_{Te}^{2+}\right]\cdot n^2 / \left[V_{Te}^0\right]$	1,56·10^{30}·T^3	0,02

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IV	$V_{Pb}^{0} = V_{Pb}^{-} + h^{+}$	$K_b = \left[V_{Pb}^{-}\right] \cdot p / \left[V_{Pb}^{0}\right]$	$1{,}83 \cdot 10^{15} \cdot T^{3/2}$	0,01
V	$V_{Pb}^{0} = V_{Pb}^{2-} + 2h^{+}$	$K_b^{/} = \left[V_{Pb}^{2-}\right] \cdot p^2 / \left[V_{Pb}^{0}\right]$	$3{,}35 \cdot 10^{30} \cdot T^{3}$	0,02
VI	$"0" = e^{-} + h^{+}$	$K_i = n \cdot p$	$7{,}42 \cdot 10^{29} \cdot T^{3}$	0,38
VII	$2\left[V_{Pb}^{2-}\right] + \left[V_{Pb}^{-}\right] + n = 2\left[V_{Te}^{2+}\right] + p$			

$K = K_0 \exp(-\Delta H / kT)$ – equilibrium constant; P_{Te_2} – partial vapour pressure of tellurium; e^{-} – electrons; h^{+} – holes; n and p – concentration of electrons and holes, respectively; $"v"$ – vapour.

Reaction (I) describes the formation of neutral cationic and anionic vacancies, and (II) – neutral vacancies of lead in the interaction with a vapour of tellurium, (III)-(V) – reactions of ionization of formed defects, (VI) – reaction of excitation of intrinsic conductivity. Equation (VII) – overall condition of electro neutrality of the crystal.

Equilibrium constants were calculated using the band theory of non degenerate semiconductors, and approximation of experimental data of the homogeneity region of PbTe. Solving combined quasi chemical equations analytical dependences of concentration of current carriers and point defects on the annealing temperature and partial vapour pressure component were found.

At low partial pressures of tellurium vapour P_{Te_2} and high annealing temperature T crystals of n-type conductivity are obtained. With increasing partial pressure of tellurium vapour at constant annealing temperature electron density decreases, and at a certain vapour pressure of tellurium conductivity changes from n-to p-type and further the concentration of holes increases (Figure 2).

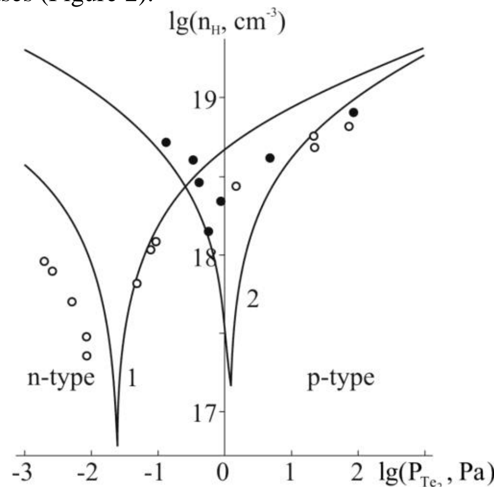

Fig 2. Dependences of Hall concentration of current carriers n_H on the partial vapour pressure of tellurium P_{Te_2} at annealing temperature T: 1 – 918 K, 2 – 1053 K. Curves – calculation. Points – experimental data [7]

At low annealing temperature T and high partial pressures of tellurium vapour P_{Te_2} crystals of p-type conductivity are obtained. With increasing annealing temperature at a constant partial vapour pressure of tellurium hole concentration decreases and at certain temperature inversion of conductivity from p- to n-type occurs and the electron concentration begins to increase (Figure 3).

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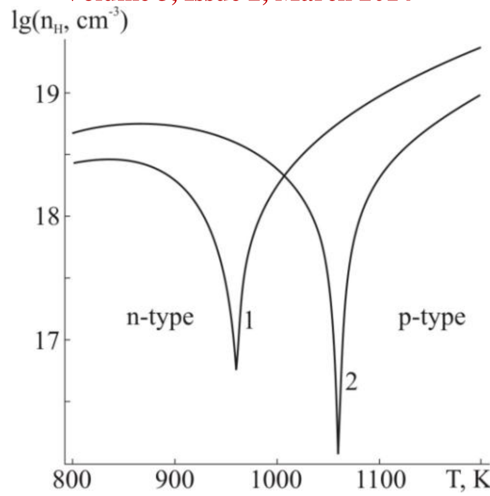
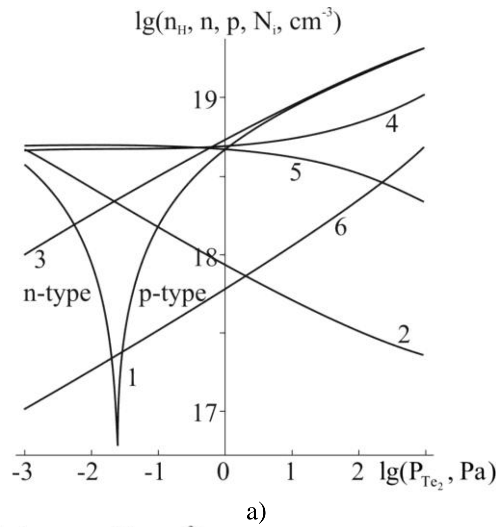
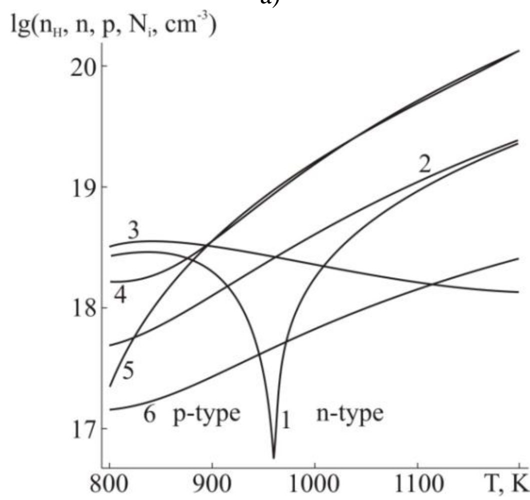


Fig 3. Dependences of Hall concentration of current carriers n_H on annealing temperature T at the partial vapour pressure of tellurium P_{Te_2} : 1 – 0.086 Pa, 2 – 1.396 Pa



a)



b)

Fig 4. Dependences of Hall concentration (1 – n_H), concentration of current carriers and ionized point defects on partial vapour pressure of tellurium (T = 918 K) (a) and on the annealing temperature T of lead telluride crystals (P_{Te_2} = 0.086 Pa) (b): 2 – n, 3 – p, 4 – [V_{Pb}^{2-}], 5 – [V_{Te}^{2+}], 6 – [V_{Pb}^{1-}]

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Increasing the partial pressure of tellurium vapour at constant annealing temperature leads to increase of hole concentration (Figure 4, a – curve 3), the electron concentration in the crystal decreases (Figure 4, a – curve 2), which leads to a change of the conductivity type (Figure 4, a – curve 1). This is due to increasing concentration of single- and doubly charged vacancies of lead (Figure 4, a – curves 4, 6) and decrease of concentration of tellurium vacancies (Figure 4, a – curve 5) with the increase of the partial vapour pressure of tellurium. Calculation of concentration of current carriers and ionized defects shows that at low annealing temperatures doubly ionized vacancies of lead V_{Pb}^{2-} dominate (Figure 4, b – curve 4). With increasing temperature the concentration of defects increases and fastest – V_{Te}^{2+} (Figure 4, b – curve 5), which explains the temperature trend of a curve n_H (Figure 4, b – curve 1).

C. Thermodynamic Approache

The equilibrium concentration of point defects determined by thermodynamic potentials provided equality of chemical potentials μ of each component in gas (g) and crystal (s) of heterogeneous system at given temperature T:

$$\mu_i^s = \mu_i^g , \tag{9}$$

The chemical potential of vapour is [4]:

$$\mu^g = kT \ln P + \mu_0 . \tag{10}$$

To determine the chemical potential of defects that are equal to the chemical potential of component taken with the sign "+" or "–" in the crystal method of differentiation of Gibbs energy G to the concentration of the defect was used. Gibbs energy is represented as:

$$G = G_0 + \sum (E + F_{vib})[D] + nE_C - pE_V - T(S_n + S_p + S_k), \tag{11}$$

where G_0 – Gibbs energy that does not depend on the presence of defects, E – energy of defect formation, F_{vib} – free vibrational energy of defect D, $[D]$ – defect concentration, n and p – concentration of electrons and holes, respectively, E_C, E_V – energy of conduction-band bottom and valence band top, respectively, S_k – configuration entropy, S_n, S_p – entropy of electrons in the conduction band and holes in the valence band, respectively. The summation is over all sub lattices and all defects in sub lattice.
Energies of singly and doubly ionized defects are determined by the formulae:

$$E_1 = E_0 - \frac{Z}{|Z|}\varepsilon_1 ; \; E_2 = E_0 - \frac{Z}{|Z|}(\varepsilon_1 + \varepsilon_2) ,$$

Where E_0 – energy of formation of neutral defect, Z – charge state of the defect, ε_1, ε_2 – first and second levels of ionization formed defect.
The change of free vibration energy of the crystal in the formation of defect:

$$F_{vib} = \pm \left\{ 3kT \ln\left(\frac{T_\theta}{T}\right) - kT \right\} + x \cdot 3kT \ln\left(\frac{\omega}{\omega_0}\right), \tag{12}$$

Where x – number of atoms that have changed their frequency of oscillation from ω_0 to ω.
Entropy is determined by the Boltzmann law:

$$S_k = k \ln(\prod W_j) = \sum k \ln(W_j) = \sum S_j , \tag{13}$$

where W_j – thermodynamic probability of the j-th sublattice.
Given that the effective mass of electrons depends on their concentration in law:

$$m^* = m_0 \left(1 + \frac{2\mu}{E_g}\right)$$

and assuming that similar dependence is valid for the effective mass of light holes:

$$n = \left(\frac{2\pi m_{e,0}^* kT}{h^2}\right)^{\frac{3}{2}} a e^{b\frac{\mu}{kT}} \left(1 + \frac{2\mu}{E_g}\right)^{\frac{3}{2}}, \; p_l = \left(\frac{2\pi m_{h,0,l}^* kT}{h^2}\right)^{\frac{3}{2}} a e^{-b\frac{\mu + E_{g,l}}{kT}} \left(1 + \frac{2\mu}{E_g}\right)^{\frac{3}{2}},$$

$$p_h = \left(\frac{2\pi m_{h,h}^* kT}{h^2}\right)^{\frac{3}{2}} a e^{-b\frac{\mu + E_{g,2}}{kT}} .$$

The chemical potential μ of electrons can be determined from the equation of electro neutrality:

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$$\sum Z[D]=\left(\frac{2\pi m_{e,0}^{*}kT}{h^{2}}\right)^{\frac{3}{2}}ae^{b\frac{\mu}{kT}}\left(1+\frac{2\mu}{E_{g}}\right)^{\frac{3}{2}}-$$
$$-\left[\left(\frac{2\pi m_{h,0,l}^{*}kT}{h^{2}}\right)^{\frac{3}{2}}ae^{-b\frac{\mu+E_{g,l}}{kT}}\left(1+\frac{2\mu}{E_{g,l}}\right)^{\frac{3}{2}}-\left(\frac{2\pi m_{h,h}^{*}kT}{h^{2}}\right)^{\frac{3}{2}}ae^{-b\frac{E_{g,h}+\mu}{kT}}\right].$$

The summation is carried out over all ionized defects.

As such, this equation cannot be solved analytically, so to simplify this task, the experimental data [5] have been approximated by the function:

$$\frac{m^{*}}{m_{e,0}^{*}}=\alpha n^{\beta}=0{,}111\cdot10^{-6}\cdot n^{\frac{1}{3}}. \tag{14}$$

At high temperatures we can neglect the influence of light-hole band. So, given that the chemical potential of the defect in the crystal for high temperatures is defined as:

$$\mu_{D_i}^{s}=E_i+F_{vib,i}-kT\ln\left(\frac{N_J-\sum[D]}{[D]}\right)+$$
$$+\left[2n\left(E_C-kT\left(\ln\frac{N_C-n}{n}-\frac{N_C}{2n}\ln\frac{N_C-n}{N_C}\right)+p\left(E_V+kT\left(\ln\frac{N_V-p}{p}\right)\right)\right)\right]\cdot\frac{b}{kT}\frac{\partial\mu}{\partial D}. \tag{15}$$

Thus, for calculating of the equilibrium concentrations of point defects in two-temperature annealing we need to solve the combined equations (9). Each such equation is written for all point defects presented in the crystal. The combined equations have been solved by minimizing a quadratic function of the residuals using the mathematical package Maple 9.5.

According to the calculation in the material saturated with lead the dominant defects are doubly ionized tellurium vacancies V_{Te}^{2+} (Figure 5 – curve 3) and in the material saturated tellurium – singly and doubly ionized vacancies of lead (Figure 5 – curves 1, 2). At a fixed value of the annealing temperature with increasing of the vapour pressure of tellurium concentration of doubly charged vacancies of lead is growing faster than the concentration of singly charged vacancies, so that in the vicinity of *n*-*p*-conversion V_{Pb}^{2-} is the dominant defect (Figure 5 – curve 2) and at the maximum vapour pressure of tellurium the dominant defect is V_{Pb}^{1-} (Figure 5 – curve 1).

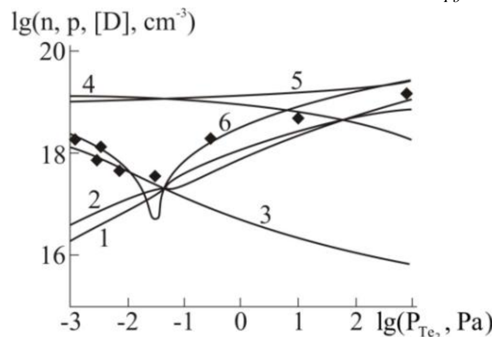

Fig 5. Dependences of the concentration of point defects [*D*] (1 – V_{Pb}^{1-}; 2 – V_{Pb}^{2-}; 3 – V_{Te}^{2+}), electrons (4 – *n*), holes (5 – *p*) and Hall concentration (6 – n_H) of PbTe on partial vapour pressure of tellurium P_{Te_2} at the two-temperature annealing at 918 K. Curves – calculation. Points – experimental data [8]

The dependence of the concentration of point defects and current carriers on temperature is shown in Figure 6 at maximum vapour pressure of tellurium in the high-temperature equilibrium.

Theoretically determined concentration of current carriers describes the experimental data satisfactorily. Concentrations of neutral lead vacancies and neutral and singly ionized tellurium vacancies are much smaller than the concentration of other considered defects, through which the graph of their dependencies is not given.

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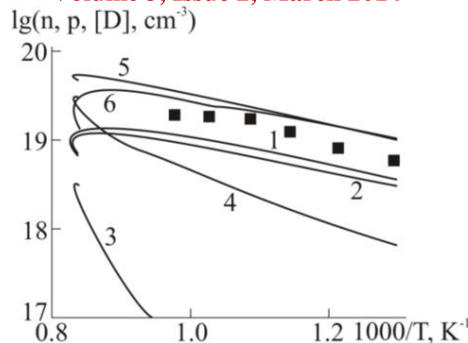

Fig 6. Dependences of the concentration of point defects [*D*] (1 – V_{Pb}^{1-} ; 2 – V_{Pb}^{2-} ; 3 – V_{Te}^{2+}), electrons (4 – *n*), holes (5 – *p*) and Hall concentration (6 – n_H) of PbTe on annealing temperature *T* at the maximum partial vapour pressure of tellurium P_{Te_2} in the high-temperature equilibrium. Curves – calculation. Points – experimental data [8]

D. Calculation of the homogeneity region of PbTe

Using different methods of determination of the concentration of excess components leads to significant variation in the experimental data (Figure 7). The narrowest region of homogeneity of the crystals was obtained using traditional indirect methods of its determining when solidus line was built on the basis of the low-temperature values of various physical parameters of crystals, reduced to some equilibrium state at high temperatures [6]. The most extensive homogeneity region of PbTe was determined by high-temperature measurements of the Hall coefficient and conductivity coefficient, synchronous with heat treatment. The difference between low-temperature and high-temperature measurements can be associated with the transition of the excess component in the electro neutral condition [6].

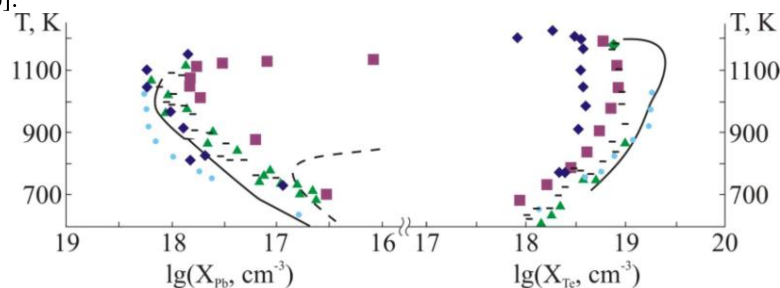

Fig 7. *T-X*$_{Te}$ diagram of PbTe in the homogeneity region of compound. Curves – calculation (solid – subject to dependence $m_e^*(n)$, dashed – without this dependence). Points – experimental data (♦ – [9], ■ – [10], ▲ – [11], ● – [8], ▬ – [12]).

Using the method of the thermodynamic potentials the homogeneity region of PbTe crystals was calculated (Figure 7). The maximum calculated value of the deviation from stoichiometry on the side of excess lead is $dX_{Pb} \approx 1{,}4\cdot10^{18}$ cm^{-3} at $T = 1013$ K, and on the side of excess tellurium – $dX_{Te} \approx 2{,}5\cdot10^{19}$ cm^{-3} at $T = 1132$ K, which agrees well with the presently known literature data. It should be noted that the model accurately describes the data of Hall measurements and temperature dependence of the solidus line of excess lead and excess tellurium, which may be evidence of its adequacy.

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ISSN: 2319-5967
ISO 9001:2008 Certified
International Journal of Engineering Science and Innovative Technology (IJESIT)
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