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**Point Defects and Physicochemical Properties of Crystals in Pb-Sb-Te System**

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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-Sb:Te: substitution of antimony ions into lead sites $Sb_{l}^{n}$ with the formation of cation vacancies $V_{c}^{m}$ (I) or neutral interstitial tellurium atoms $Te_{i}^{0}$ (II) were examined. Dominant point defects in doped crystals PbTe:Sb and PbTe-Sb$_{x}$Te$_{3-x}$ solid solutions based on p-type 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.

**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 ($\chi = 2.09 \times 10^{-5} W/K\cdot cm$), relatively high current carrier mobility ($\mu = 10^{4} cm^{2} V^{-1} s^{-1}$), the largest value of $\mu\chi^{-1}$, which causes a significant thermoelectric figure of merit ($Z_{max} = Z = a'/\sigma\chi$, where $a'$ – coefficient of thermo-emf, $\sigma$ – electrical conductivity, $\chi$ – coefficient of thermal conductivity. Clearly, large $Z$ (which determined commercial use of thermoelectric material) depends on $\alpha$ and $\sigma$, which are sensitive to the nature of electronic states. Thermal conductivity is defined by phonon spectrum of the crystal ($\chi_{p}$) and the concentration of current carriers ($\chi_{e}$). Decrease of thermal conductivity components ($\chi = \chi_{p} + \chi_{e}$) 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$^{IV}$-Ge, Sn, Pb; C$^{V}$- Bi, Sb; B$^{VI}$- Te) [2].

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 [3].

The type of PbTe-Sb diagram is eutectic. The solubility of Sb in PbTe at 820 K is 1.5 at. % [4]. Antimony, acting as a donor, moves homogeneity region limits toward higher equilibrium concentrations [5]. Solubility of Sb$_{x}$Te$_{3}$ in PbTe for PbTe-Sb$_{x}$Te$_{3}$ is defined in [6-8]. At lower temperatures (573-823 K) solubility is about (2-4) at. % of Sb [7, 8]. The maximum solubility (~6 at. % Sb) obtained in the research of crystallization of PbTe-Sb$_{x}$Te$_{3}$ [9] is higher than the solubility at lower temperatures. According to [10], the boundary region of Sb$_{x}$Te$_{3}$ solubility in PbTe is approximately 2 mole %, and in [7, 11] – (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.

I. Crystal-Quasichemical Modeling

1.1. Doped Crystals p-PbTe:Sb

1.1.1. Analysis of Dopant Behavior. Taking into account that the valence shell of atoms of V group elements has \( s^2p^6 \) configuration, Sb atoms can give \( s^2p^6 \) configuration, valence +3) or accept \( s^2p^6 \) configuration, valence –3) electrons from \( p \)-state. So dopant in PbTe can be in two charge states \( Sb^{3+} \) and \( Sb^{5+} \). 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. Thus, in doped crystals PbTe:Sb dopant, replacing lead in its sublattice, ionizes from state \( Sb^{2+} \) and is an acceptor, while relatively \( Te^{2-} \) sublattice dopant is in state \( Sb^{5+} \). 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:

\[
Sb^5+ \rightarrow Sb^{3+}_p + Sb^{3+}_T + 3(l-z)e^- + 3zh^+.
\]

Here \( z = \frac{[Sb^{3+}_p]}{[Sb^{3+}_T] + [Sb^{5+}_T]} \) – the value of disproportionation of dopant charge state \( (0 \leq z \leq 1) \), where \( e^- \) - electrons, \( h^+ \) - holes.

The relation between \( [Sb^{3+}_p] \) and \( [Sb^{5+}_T] \) determine donor or acceptor dopant effect.

1.1.2. Crystalquasichemical Formulae. For the analysis of the defect subsystem in investigated crystals crystalquasichemical approach was used. It is based on the concept of antistructure, which has the form of the 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:

\[
V_{pb}^n V_{te}^\ast + Sb^5+ \rightarrow \left[ V_{pb}^{n\ast} Sb^\ast \right]_{pb} \left[ V_{te}^{\ast\ast} Sb^\ast \right]_{te} + 3(l-z)e^- + 3zh^+.
\]

Crysta...
Then crystalquasichemical formula of p-PbTe-
Sb$_2$Te$_3$ is:

$$V_{\text{p}}^+/V_{\text{e}}^- + \text{Sb}^{2+}_{\frac{1}{2}}\text{Te}^{0}_{\frac{3}{2}} \rightarrow \begin{bmatrix} \text{Sb}^+ \frac{1}{2} V^+_{\text{p}} \text{\_Te}^0_{\frac{1}{2}} \end{bmatrix} + \text{Te}^+_{\text{e} \_p}.$$

(5)

Then crystalquasichemical formula of p-PbTe-
Sb$_2$Te$_3$ is:

$$\begin{bmatrix} \text{Pb}^+_{\frac{1}{2}-(1-x)-x} \text{Sb}^+_{\frac{1}{2}-(1-x)+x} V^+_{\text{p} \_ \text{e}} \end{bmatrix} \_\text{p} \begin{bmatrix} \text{Te}^+_{\frac{1}{2}-(1-\beta)(1-x)+x} V^+_{\beta \_ \text{e}} \end{bmatrix} \_\text{e} + \beta(2-2\gamma-\delta)(1-x) h^+ + x e^-.$$

(6)

where $x$ – molar fraction of Sb$_2$Te$_3$.

**1.2.2. Mechanism II.** At calculation per 1 Sb atom
and subject to charge state of Sb$^{3+}$ and Te$^{2-}$ ions chemical
formula for alloying components is written as:

$$V_{\text{p}}^+/V_{\text{e}}^- + \text{Sb}^{2+}_{\frac{1}{2}}\text{Te}^{0}_{\frac{3}{2}} \rightarrow \text{Sb}^+_{\text{p} \_ \text{e}}\text{Te}^+_{\text{e} \_p}.$$

(7)

Then crystalquasichemical formula of p-PbTe-
Sb$_2$Te$_3$ is:

$$\begin{bmatrix} \text{Pb}^+_{\frac{1}{2}-(1-x)-x} \text{Sb}^+_{\frac{1}{2}-(1-x)+x} V^+_{\text{p} \_ \text{e}} \end{bmatrix} \_\text{p} \begin{bmatrix} \text{Te}^+_{\frac{1}{2}-(1-\beta)(1-x)+x} V^+_{\beta \_ \text{e}} \end{bmatrix} \_\text{e} + \beta(2-2\gamma-\delta)(1-x) h^+ + x e^-.$$

(8)

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**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

$$n + q_{\text{V}_{\text{e}}} [V_{\text{p}}^+] + q_{\text{V}_{\text{e}}} [V_{\text{p}}^+] + q_{\text{V}_{\text{e}}} [\text{Sb}^+_{\text{e} \_p}] = p + q_{\text{V}_{\text{e}}} [V_{\text{e}}^+] + q_{\text{V}_{\text{e}}} [\text{Sb}^+_{\text{p} \_e}],$$

(9)

where $p = A(\beta(2-2\gamma-\delta)(1-x)+3zx)$,
$n = 3A(1-z) x$, $[\text{Sb}^+_{\text{e} \_p}] = Ax$, $[V_{\text{p}}^+] = A(1-x)$,
$[V_{\text{e}}^+] = A(1-\beta(1-x)+x)$, $[\text{Sb}^+_{\text{e} \_p}] = A(1-z) x$,
$[\text{Sb}^+_{\text{p} \_e}] = A(1-\beta(1-x)+1-z)x$,
$q_{\text{V}_{\text{e}}} = q_{\text{Sb}^+_{\text{e} \_p}} = q_{\text{Sb}^+_{\text{p} \_e}} = 1$, $q_{\text{V}_{\text{e}}} = q_{\text{V}_{\text{e}}} = 2$.

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

Hall concentration of current carriers $n_{\text{H}}$ in this case is defined as:
n_H = A[\beta(1-z)x - \beta(2-2\gamma - \delta)(1-x) - 3zx]. 

(10)

Similar analysis was done for PbTe-Sb\textsubscript{2}Te\textsubscript{3} solid solution.

II. Results and Discussion

2.1. Doped Crystals p-PbTe:Sb

In doped PbTe:Sb crystals when the value of \( z < 0.5 \) admixture does donor action ([Sb\textsubscript{p\textsubscript{n}}\textsuperscript{+}\textsubscript{i}] > [Sb\textsubscript{p\textsubscript{ni}}\textsuperscript{+}\textsubscript{i}]): 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\textsubscript{p\textsubscript{n}}\textsuperscript{+}\textsubscript{i}] < [Sb\textsubscript{p\textsubscript{ni}}\textsuperscript{+}\textsubscript{i}]) 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\textsubscript{p\textsubscript{n}}\textsuperscript{+}\textsubscript{i}] = [Sb\textsubscript{p\textsubscript{ni}}\textsuperscript{+}\textsubscript{i}]), 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).

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

![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 (\( z \)).](image1.png)

![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 – \( \text{Sb}^{+2}_{\text{p}} \); 3 – \( \text{Sb}^{+2}_{\text{t}} \); 4 – \( \text{V}^{+2}_{\text{p}} \); 5 – \( \text{V}^{+2}_{\text{t}} \); 6 – \( \text{V}^{+2}_{\text{t}} \); 7 – \( \text{Te}^{0} \) (\( z = 0.45 \)).](image2.png)

The proposed mechanism of doping satisfactorily explains the experimentally observed behavior of thermoelectric parameters on dopant content. Thus, based on the data of \([15-17]\) we can conclude that, in practice, there is realization of condition: \( z < 0.5 \), i.e. the concentration of impurity ions \([\text{Sb}^{+2}_{\text{p}}] \) overrides \([\text{Sb}^{+2}_{\text{t}}] \). Specifically, comparing the experimental data \([15]\) 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: \( z = 0.45 \) 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 \([\text{Sb}^{+2}_{\text{t}}] < [\text{Sb}^{+2}_{\text{p}}] \).  

2.2. Solid Solutions p-PbTe-Sb\textsubscript{2}Te\textsubscript{3}

Thermoelectric parameters of PbTe-Sb\textsubscript{2}Te\textsubscript{3} were studied in several papers \([2, 6, 7, 11, 18]\). In \([7]\) it was found that the increase of Sb\textsubscript{2}Te\textsubscript{3} content in solid solution leads to donor effect with microhardness increase (H) (Fig. 4 – curve 1) and decrease of the coefficient of thermo-emf (\( \alpha \)) (Fig. 4 – curve 3). In alloys containing Sb\textsubscript{2}Te\textsubscript{3} more (1.5-2) mole % Hall concentration \( n_H \) (Fig. 4 – curve 2) and thermo-emf \( \alpha \) (Fig. 4 – curve 3) practically do not change. Issues associated with the decrease of the value of thermal conductivity of PbTe-Sb\textsubscript{2}Te\textsubscript{3} solid solutions with Sb\textsubscript{2}Te\textsubscript{3} content increase were studied in \([5, 18]\). The value of \( \chi \) for alloy of PbTe with 1.02 mole % Sb\textsubscript{2}Te\textsubscript{3} is 1.25·10\textsuperscript{-5} WK\textsuperscript{-1}cm\textsuperscript{-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 \( (\gamma_1) \) and electron \( (\gamma_2) \) components of thermal conductivity \([2]\).
Consider in detail the mechanisms of defect formation in PbTe-Sb$_2$Te$_3$ solid solutions. When realization of mechanism I (stoichiometry for chalcogen) there is slight decrease of concentration of major current carriers with Sb$_2$Te$_3$ fraction increase (Fig. 5, a – curve 1). With realization of mechanism II (stoichiometry for antimony) in p-PbTe-Sb$_2$Te$_3$ (Fig. 5, b – curve 1) with Sb$_2$Te$_3$ 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 Sb$_2$Te$_3$ (Fig. 4 – curve 2), we can conclude that when the dopant content to 2 mole % of Sb$_2$Te$_3$ mechanism II is dominant, and with more of its contents (up to the limit of solubility) mechanism I is dominant.

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$_2$Te$_3$ crystals with Sb$_2$Te$_3$ content increase there is significant increase of the concentration of ionized antimony in lead sites Sb$^{1+}_p$ (Fig. 5, a – curve 2) and
doubly charged cation vacancies $V_{Pb}^{2+}$ (Fig. 5, a – curve 3). Concentrations of $V_{Pb}^{2+}$, $V_{Te}^{2+}$, Te$^0$ decrease slightly (Fig. 5, a – curves 4, 5, 7). For mechanism II in p-PbTe:Sb$_1$Te$_2$ crystals the dominant defects are Sb$_{Pb}^{1+}$, Te$_{Pb}^{0}$, $V_{Pb}^{2+}$ (Fig. 5, b). Concentrations [Sb$_{Pb}^{1+}$] and [Te$^0$] increase with dopant content increase (Fig. 5, b – curves 2, 7), and $[V_{Pb}^{2+}]$ decreases slightly (Fig. 5, b – curve 3). Point defects $V_{Pb}^{0}$ and $V_{Te}^{2+}$ do not significantly affect the conductivity. Concentration of $V_{Pb}^{1+}$ and $V_{Te}^{2+}$ does not change with Sb$_2$Te$_3$ content increase (Fig. 5, b – curves 4, 5). Thus, the contribution to the conductivity of substitution defects Sb$_{Pb}^{1+}$ increases, and $V_{Pb}^{0}$ decreases with dopant content increase.

Conclusions

1. 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 $[\text{Sb}_{Pb}^{1+}] > [\text{Sb}_{Te}^{1+}]$, dopant is the donor, and with prevalence of Sb in anion sites $([\text{Sb}_{Pb}^{1+}] < [\text{Sb}_{Te}^{1+}])$ dopant is the acceptor, and when $[\text{Sb}_{Pb}^{1+}] = [\text{Sb}_{Te}^{1+}]$ there is a complete self-compensation of influence of dopant.

2. It has been shown that in doped crystals PbTe:Sb experimental results are explained satisfactorily provided $[\text{Sb}_{Pb}^{1+}] > [\text{Sb}_{Te}^{1+}]$. 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.

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

4. It has been shown that with increasing content of alloying compound in PbTe-Sb$_2$Te$_3$ solid solutions to 2 mole % of Sb$_2$Te$_3$ 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$_2$Te$_3$.

5. 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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Точкові дефекти і фізико-хімічні властивості кристалів у системі Pb-Sb-Te

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 іонами стибію позицій плюмбуму Pb⁺⁺ з утворенням катіонних вакансій V⁺⁺ (I) або нейтральних атомів теллу в міжвузлі (II). Визначені домінуючі точкові дефекти у легованих кристалах PbTe:Sb і твердих розчинах PbTe-Sb₂Te₃ на основі p-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.