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Defect Subsystem of $\text{Pb}_{1-x}\text{Ag}_x\text{Te}$ Solid Solutions

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In the framework of crystalloquasichemical formalism, the mechanism of formation of $\text{Pb}_{1-x}\text{Ag}_x\text{Te}$ solid solutions has been considered. The dependences of Hall concentration and the concentration of point defects on composition of solid solution and the value of disproportionation of the charge state of impurity defects have been calculated.

Key words: solid solution, point defects, crystalloquasichemical formalism, lead telluride.

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Introduction

Lead telluride is promising thermoelectric material for the mid-temperature region. It poses a number of unique properties: multivalley nature of energy spectrum ($N = 4$), low lattice thermal conductivity ($\chi = 2.09 \cdot 10^{-2} \text{ W} \cdot \text{K}^{-1} \cdot \text{cm}^{-1}$), relatively high charge carrier mobility ($\mu \approx 10^3 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$), the largest value of $\mu\chi^{-1}$, which causes a significant thermoelectric figure of merit [1].

Lead telluride crystallizes in NaCl crystal structure, which is typical for ionic crystals (chemical bond is complex and close to the ionic-covalent-metallic). It 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) conductivity that causes significant concentration (10^{18} - 10^{19} cm^{-3}) of electrically active intrinsic defects [2].

The basic parameters of lead telluride can be changed effectively by doping and forming solid solutions. It is worth paying attention to silver, which has a number of advantages among other acceptor impurities, the behavior of which is studied insufficiently in comparison with donor impurities, in particular thallium is an extremely toxic element, and the process of doping with alkali metals causes many technological difficulties associated with the oxidation of these metals in air [3].

Performance device structures are largely determined by defect subsystem of 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 treatment of the material. Analyzing the current state of the problem, it should be noted that the ambiguity of the experimental data and theoretical clarification 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 from one standpoint remains an urgent problem.

The paper deals with the analysis of defect subsystem and mechanism of formation of $\text{Pb}_{1-x}\text{Ag}_x\text{Te}$ solid solutions based on lead telluride.

I. Crystalloquasichemical Modeling

In PbTe, $6s^2$ and $5s^2$ states of Pb and Te atoms are completely filled, and the valence and conduction bands are formed primarily out of $6p^2$ states of Pb and $5p^2$ states of Te. The Pb-Te bonds have both covalent and ionic character. The removal of one Pb atom or replacing it by a monovalent cation (e.g., Ag) leads to a local charge disturbance and alters the covalent bonding with the neighboring Te. In this case, if Ag atom gives one electron, when it substitutes Pb (which is divalent), it compensates only one hole and therefore acts as an acceptor [4].

The crystallochemical mechanism of the acceptor action of Ag has a controversial nature and is not fully studied. With the introduction of Ag atoms along with an equal number of chalcogen atoms, two silver atoms create completely saturated bonds with only one tellurium atom according to the scheme: $2\text{AgTe} = \text{Ag}_2\text{Te} + \text{Te}$. Unsaturated bonds of another Te atom determine the acceptor action, creating two holes in the valence band.

In addition, the low doping efficiency, estimated in [3], does not exceed 3% and decreases with increasing amount of impurity. X-ray analysis data [5], according to

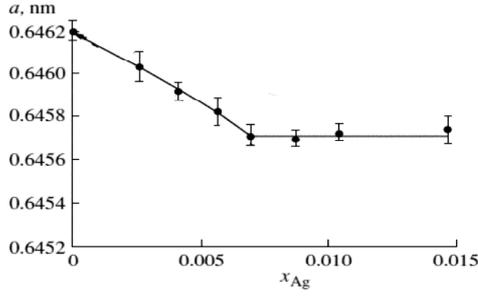
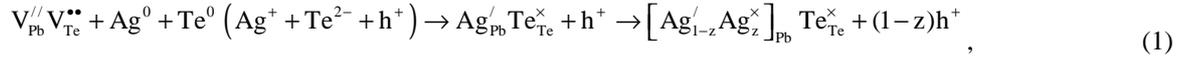


Fig. 1. Dependence of the lattice parameter of $Pb_{1-x}Ag_xTe$ solid solution on silver content [6].

which $Pb_{1-x}Ag_xTe$ are substitutional solid solutions, suggests that most introduced silver atoms are uncharged in $PbTe$ crystal lattice.

The mechanism of substitution of Pb lattice sites by Ag atoms is also confirmed by experimental data on the lattice parameter of $Pb_{1-x}Ag_xTe$ solid solutions, which



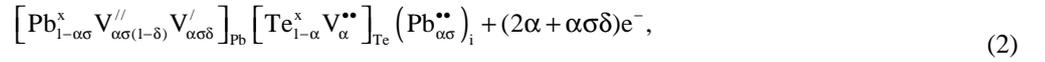
where z is the value of disproportionation of charge state of impurity defects.

Crystalloquasichemical formula of n - $PbTe$ with the

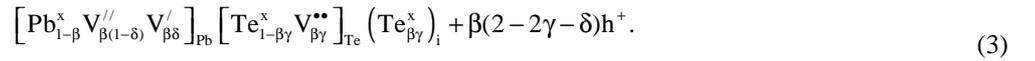
decreases with increasing silver concentration up to 0.7 mol. % and then remains unchanged, which indicates solubility limit (Fig. 1).

For the analysis of the defect subsystem of investigated crystals, crystalloquasichemical approach has been used. It is based on the concept of antistructure [7], which has the form of $V_{Pb}^{//}V_{Te}^{**}$ for lead telluride, where $V_{Pb}^{//}$ and V_{Te}^{**} are doubly charged lead and tellurium vacancies, respectively; "/" and "*" indicate negative and positive charges, respectively. Crystal formula is written as a superposition of alloying cluster formed on the basis of basic matrix antistructure and crystal formula of basic compound.

Taking into account the disordering in the cation sublattice and incorporation of Ag atoms at Pb lattice sites (Ag_{Pb}), alloying cluster can be written as follows:

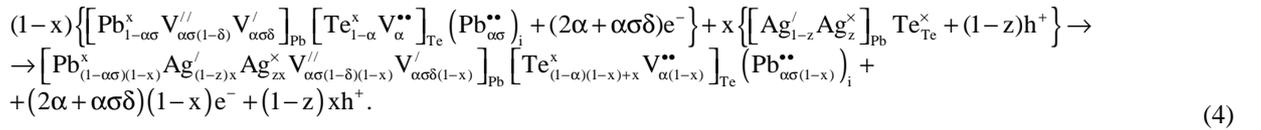


and crystalloquasichemical formula of p - $PbTe$ [8]:

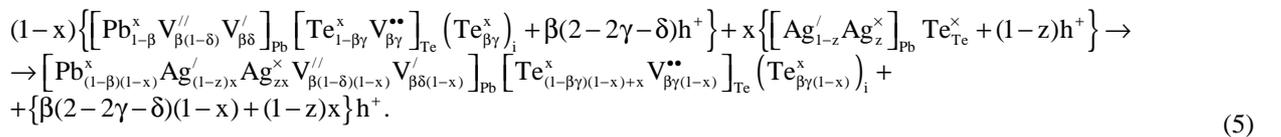


Then, the crystalloquasichemical formula of n - $Pb_{1-x}Ag_xTe$ solid solution as a superposition of

crystalloquasichemical formula of n - $PbTe$ (2) and the alloying cluster (1) is



Similarly, in the case of p - $Pb_{1-x}Ag_xTe$:



Here x is molar fraction of AgTe , e^- is an electron, h^+ is a hole, α (β) is the value of the initial deviation from stoichiometry on the side of Pb (Te), δ is coefficient of disproportionation of cationic vacancies' charge state, σ (γ) is fraction of interstitial Pb (Te), „ x ” indicates neutral charge.

The proposed mechanism of solid solution formation and crystalloquasichemical formulae (4) and (5) make it possible to find analytical dependences of the

concentration of individual point defects and free charge carriers on the value of deviation from stoichiometric composition in the base compound (α , β) and composition of solid solution (x).

In particular, for $n\text{-Pb}_{1-x}\text{Ag}_x\text{Te}$ according to crystalloquasichemical formula (4), electroneutrality condition is written as follows:

$$n + |q_{V_{Pb}''}|[V_{Pb}''] + |q_{V_{Pb}'}|[V_{Pb}'] + |q_{Ag'_{Pb}}|[Ag'_{Pb}] = p + |q_{V_{Te}''}|[V_{Te}''] + |q_{Pb_i''}|[Pb_i''].$$

Here are concentrations of electrons $n = A(2\alpha + \alpha\sigma\delta)(1-x)$, holes $p = A(1-z)x$, doubly charged lead vacancies $[V_{Pb}''] = A\alpha\sigma(1-\delta)(1-x)$, singly charged lead vacancies $[V_{Pb}'] = A\alpha\sigma\delta(1-x)$, charged silver at lead lattice sites $[Ag'_{Pb}] = A(1-z)x$, doubly charged tellurium vacancies $[V_{Te}''] = A\alpha(1-x)$, doubly charged interstitial lead $[Pb_i''] = A\alpha\sigma(1-x)$,

effective charges of point defects $|q_{V_{Pb}'}| = |q_{Ag'_{Pb}}| \approx 1$, $|q_{V_{Pb}''}| = |q_{V_{Te}''}| = |q_{Pb_i''}| \approx 2$, where $A = \frac{2Z}{a^3}$, Z is number of structural units per unit cell, a is lattice parameter.

Hall concentration of charge carriers n_H in this case is defined as

$$n_H = A[(2\alpha + \alpha\sigma\delta)(1-x) - (1-z)x]$$

Similarly for $p\text{-Pb}_{1-x}\text{Ag}_x\text{Te}$, according to (5), electroneutrality condition is

$$|q_{V_{Pb}'}|[V_{Pb}'] + |q_{V_{Pb}''}|[V_{Pb}''] + |q_{Ag'_{Pb}}|[Ag'_{Pb}] = p + |q_{V_{Te}''}|[V_{Te}''],$$

where $p = A(\beta(2-2\gamma-\delta)(1-x) + (1-z)x)$, $[V_{Pb}'] = A\beta(1-\delta)(1-x)$, $[V_{Pb}''] = A\beta\delta(1-x)$, $[Ag'_{Pb}] = A(1-z)x$, $[V_{Te}''] = A\beta\gamma(1-x)$, $|q_{V_{Pb}'}| = |q_{Ag'_{Pb}}| \approx 1$, $|q_{V_{Pb}''}| = |q_{V_{Te}''}| \approx 2$.

Hall concentration is

$$n_H = A(\beta(2-2\gamma-\delta)(1-x) + (1-z)x).$$

II. Results and Discussion

Some results of calculation of Hall concentration of free charge carriers and concentrations of predominant point defects are shown in Fig. 2 and Fig. 4.

When implementing the proposed mechanism of the formation of $n\text{-Pb}_{1-x}\text{Ag}_x\text{Te}$ solid solution, there is a decrease in the concentration of the main charge carriers, a change of the type of conductivity and an increase in the concentration of holes with increasing x (Fig. 2, a). At the same time, increasing the disproportionation of the charge state z causes the shift of the curve of the thermodynamic n - p -conversion towards an increase in AgTe content (Fig. 2, a).

For $p\text{-Pb}_{1-x}\text{Ag}_x\text{Te}$, the concentration of the main

charge carriers increases (Fig. 2, b), the value of which depends on the ratio between impurity defects Ag_{Pb}^{1-} and Ag_{Pb}^0 . Moreover, for a larger z value, the increase in the hole concentration is less intense (Fig. 2, b), therefore, this value better reflects the experimental data on the low activity of silver impurity in the solid solution [3].

The obtained dependences of the concentration of the main charge carriers in the solid solution are in good agreement with the experimental data (Fig. 3). The results of measuring the conductivity of $\text{Pb}_{1-x}\text{Ag}_x\text{Te}$ solid solutions indicate that within the silver solubility region, the conductivity slightly increases (Fig. 3, a): quite quickly at $x = (0-0.003)$, and then the growth of electrical conductivity slows down, and at $x = (0.003-0.007)$ it increases very slightly. The dependence of the Seebeck coefficient for $\text{Pb}_{1-x}\text{Ag}_x\text{Te}$ solid solutions on the silver content within its solubility area shows that the starting material PbTe and all $\text{Pb}_{1-x}\text{Ag}_x\text{Te}$ solid solutions had a hole-type conductivity, and an increase in Seebeck coefficient with an increase in the silver content indicates an increase in the hole concentration, and, therefore, the acceptor nature of the impurity (Fig. 3, b).

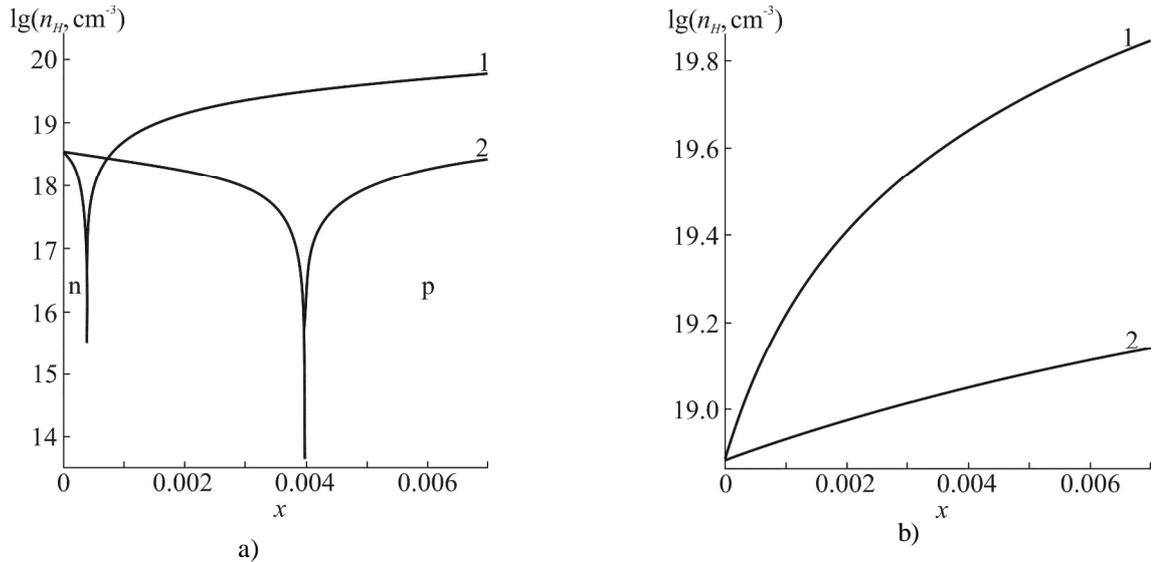


Fig. 2. Dependences of Hall concentration of charge carriers n_H for n- $\text{Pb}_{1-x}\text{Ag}_x\text{Te}$ (a) and p- $\text{Pb}_{1-x}\text{Ag}_x\text{Te}$ (b) crystals on x for different values of the disproportionation of the charge state of impurity defects z : 0.7 (1); 0.97 (2).

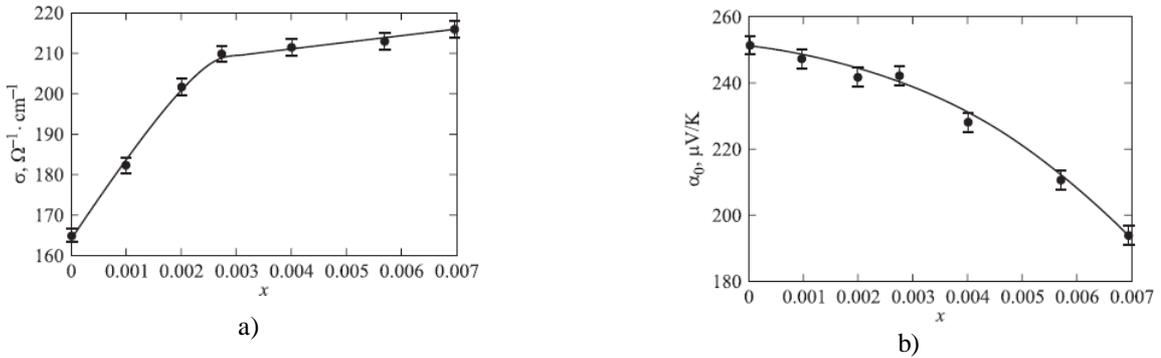


Fig. 3. Dependence of electrical conductivity σ (a) and Seebeck coefficient α_0 (b) of $\text{Pb}_{1-x}\text{Ag}_x\text{Te}$ solid solutions on x [9].

The features observed in the change in the concentration of charge carriers are associated with the ratios between individual point defects (Fig. 4). So, for both n- $\text{Pb}_{1-x}\text{Ag}_x\text{Te}$ and p- $\text{Pb}_{1-x}\text{Ag}_x\text{Te}$, the predominant defects are silver impurity atoms in cationic lattice sites $\text{Ag}_{\text{Pb}}^{1-}$ and Ag_{Pb}^0 , concentrations of which increase with x (Fig. 4, curves 1, 2).

In the case of n- $\text{Pb}_{1-x}\text{Ag}_x\text{Te}$ at $x < 0.002$, the donor centers associated with anion vacancies $\text{V}_{\text{Te}}^{2+}$ are predominant (Fig. 4, a, curve 3). When the content of AgTe is more than ~ 0.2 mol. % acceptor defects associated with $\text{Ag}_{\text{Pb}}^{1-}$ prevail (Fig. 4, a, curve 2). Thus, the change in the ratios between point defects $\text{Ag}_{\text{Pb}}^{1-}$ and $\text{V}_{\text{Te}}^{2+}$ causes the acceptor nature of the silver impurity: a decrease in the electron concentration, a change of the conductivity from n- to p-type, and a further increase in hole concentration (Fig. 2, a). It should be noted that the

contribution of intrinsic defects Pb_i^{2+} , $\text{V}_{\text{Pb}}^{2-}$, $\text{V}_{\text{Pb}}^{1-}$ is much smaller, and their concentrations remain practically unchanged with changing the impurity content (Fig. 4, a, curves 4, 5, 6).

In p- $\text{Pb}_{1-x}\text{Ag}_x\text{Te}$, doubly charged cation vacancies $\text{V}_{\text{Pb}}^{2-}$ have a sufficiently high concentration, which is almost unchanged (Fig. 4, b, curve 4). Concentrations of point defects $\text{V}_{\text{Te}}^{2+}$, $\text{V}_{\text{Pb}}^{1-}$, Te_i^0 are small, and their change with increasing x is insignificant (Fig. 4, b, curves 3, 5, 7).

The experimentally observed slowdown in an increase in electrical conductivity at $x > 0.003$ (Fig. 3, a) can be explained by a change in the ratio between impurity defects $\text{Ag}_{\text{Pb}}^{1-}$ and Ag_{Pb}^0 , in particular, by an insignificant increase in the fraction of uncharged defects.

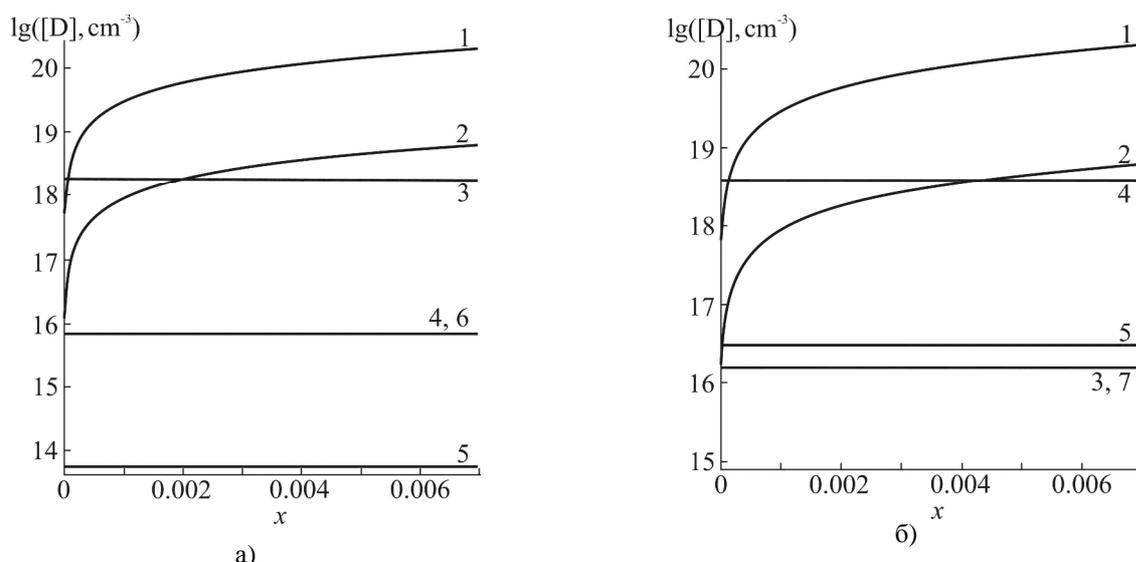


Fig. 4. Dependences of concentrations of point defects [D] for n-Pb_{1-x}Ag_xTe (a) and p-Pb_{1-x}Ag_xTe (b) crystals on x for the value of the disproportionation of Ag_{Pb} charge state $z = 0.97$: 1 – [Ag_{Pb}⁰], 2 – [Ag_{Pb}¹⁻], 3 – [V_{Te}²⁺], 4 – [V_{Pb}²⁻], 5 – [V_{Pb}¹⁻], 6 – [Pb_i²⁺], 7 – [Te_i⁰].

Conclusions

1. Crystalloquasichemical formulae for n- and p-Pb_{1-x}Ag_xTe nonstoichiometric crystals, which take into account the complex spectrum of point defects in lead telluride and disproportionation of the charge state of impurity defects, have been proposed.

2. It has been established that the crystallochemical mechanism of formation of Pb_{1-x}Ag_xTe solid solutions is associated with silver ions incorporated at lead lattice sites.

3. Based on the crystalloquasichemical formulae, the dependences of the Hall concentration of charge carriers and concentrations of individual point defects of solid solutions on the composition have been calculated.

4. It has been shown that the predominant defects

in this case are silver atoms at the cation lattice sites of lead telluride Ag_{Pb}¹⁻ and Ag_{Pb}⁰, the ratio of which determines the nature of changes in Hall concentration of charge carriers. Also, in n-type crystals, doubly charged tellurium vacancies V_{Te}²⁺ prevail, and in p-type crystals – doubly charged lead vacancies V_{Pb}²⁻.

5. The conditions for the thermodynamic n-p-conversion in Pb_{1-x}Ag_xTe solid solutions have been found.

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Дефектна підсистема твердих розчинів $\text{Pb}_{1-x}\text{Ag}_x\text{Te}$

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У рамках кристалоквазіхімічного формалізму розглянуто механізм утворення твердих розчинів $\text{Pb}_{1-x}\text{Ag}_x\text{Te}$. Розраховано залежності холлівської концентрації та концентрації точкових дефектів від складу твердого розчину і величини диспропорціювання зарядового стану домішкових дефектів.

Ключові слова: твердий розчин, точкові дефекти, кристалоквазіхімічний формалізм, шлюмбум телурид.