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Defects in Nonstoichiometric Tin Telluride at Tetra- and Octahedral Situations of Indium

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The relation of a defects formation of the solid solution SnTe-In versus a dose of dopant impurity is investigated. The crystalloquasichemical mechanism of solid solutions formation is proposed. Correlation between the hole concentration, number of point defects in the compounds and nature of defect formation processes was found. The concentration dependences of charge carriers and point defects are constructed

Keywords: tin telluride, solid solutions, crystalloquasichemical mechanism, crystalloquasichemistry, crystalloquasichemical cluster, defect formation, antistructure.

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I. Introduction

One of fundamental problems of solid-state physics is prevision of combination of the basic properties (structural, electrophysics, thermoelectrics) of materials, which one is determine by its structure, with the purpose of further control of these properties. The investigations of structural properties can gives the useful information in case when there is sufficient number of the defects in the crystals. Therefore, the investigation of the defect crystals with the large range of nonstoichiometric phase is very vital question. The tin telluride and solid solutions based on its are ideal materials for this investigations. SnTe is characterized by the broad (~0,9-1 at.%) one-sided homogeneity range, displaced in the party of an excess of a tellurium. The maximum on a solubility curve responds to composition 50,4 at.% Te (Sn_{0,984}Te) [1].

II. Experimental

The solid solutions of the system

Sn_{0,984}Te-In were investigated. The alloys synthesized from compounds of semiconducting scale of purity (not less than 99,99 % of the basic component) in evacuated up to 10⁻³ Pa quartz ampulas at 1270 K. After air cooling the samples yielded to the homogeneous annealing at 570 K during 300 hours. The basic material had p-type conductivity with a hole concentration 5,6 · 10²⁰ cm⁻³ and lattice parameter (6,312±0,0002) · 10⁻⁸ cm. The compounds with a doses up to 1 at. % In through 0,1 at.% were prepared. By the microstructural and X-ray scattering are established, that all of them lie in borders of homogeneity range and crystallize in rocksalt-structure, as well as basic SnTe. X-ray analysis was made by the precision method in CuK_α-radiation on the installation DRON-2, using a nickelous monochromator. Lattice parameter was calculated from the corrected positions of 14 diffraction lines by a computer minimization. By Hall constant measurements the carrier

concentrations was calculated using the formula

III. Crystalloquasychemical Approach to

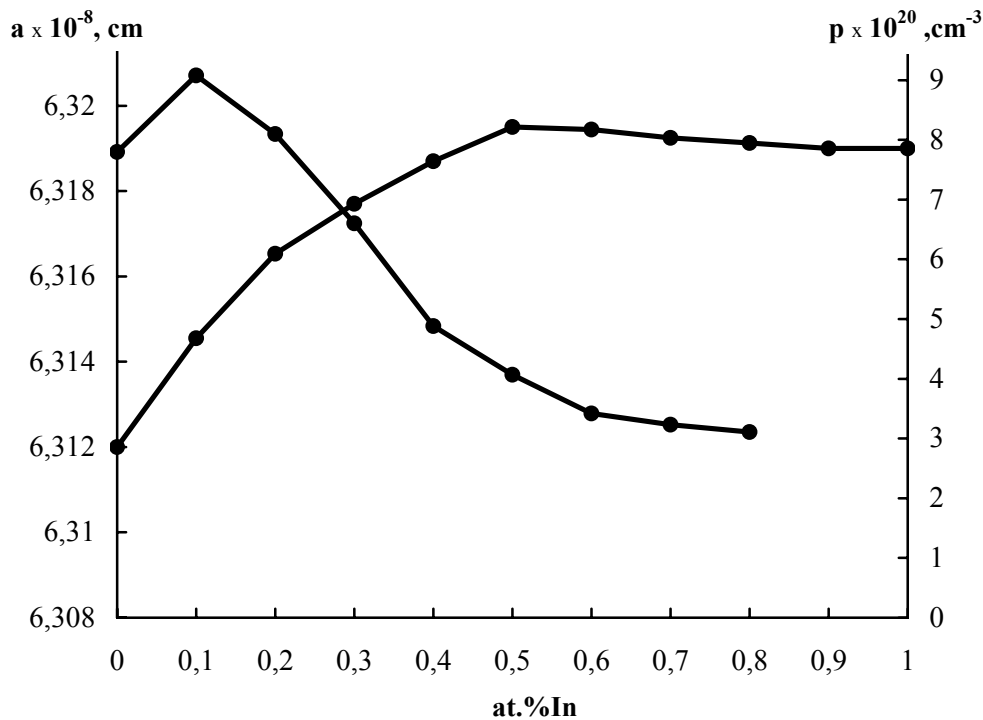


Fig. 1. Concentration dependences of lattice parameter a_0 and Hall concentrations p from In dose.

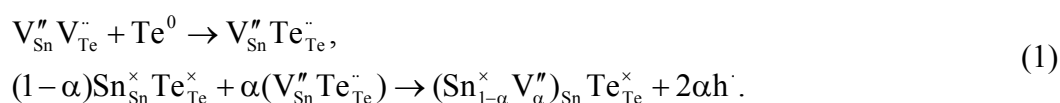
$p=r/R_{\text{HE}}$, where $r=0,6$ – Hall factor.

Observed data of lattice parameter and Hall concentrations investigations showed on the Fig. 1.

As we see, the concentration dependences have nonmonotone nature. The analysis of the obtained data demonstrates, that in small concentrations interval of an impurity (up to $\sim 0,2$ at. % In) the lattice parameter and Hall concentration increase sharply. At further increase of In dose the concentration of carriers decreases, and the increase of lattice parameter is slowed down. As result – on concentration dependences the maximum are observed ($\sim 0,2$ at.% In for p and $\sim 0,45$ at. % In for a_0). The extreme nature of concentration dependences, is most probably, testifies to change of entering of In impurity in matrix of SnTe. On the part, where the considerable deformation crystalline lattice is watched the mechanism of interstitial, on other case – mechanism of substitution.

Study of a Defect-Formation Mechanism

In the given report for the first time applied crystalloquasichemical method for the description of defect formation processes in compounds as $A^{IV}B^{VI}$, that make it possible to study and to predict of the nonstoichiometry, nature of defective states and reaction mechanisms for the participation of crystalline materials. This method bases on the information on a crystalline constitution of material. The essence it consists in



Where V_{Sn}'' – doubly ionized negative vacancy of the tin (cationic vacancy),

V_{Te}'' – doubly ionized positive vacancy of the tellurium (anionic vacancy)

α – deviation from a stoichiometry.

As we see, nonstoichiometry of tin monotelluride connected with an excess of a tellurium and conditioned by cationic vacancies.

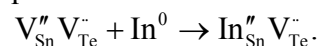
IV. Defect formation at doping

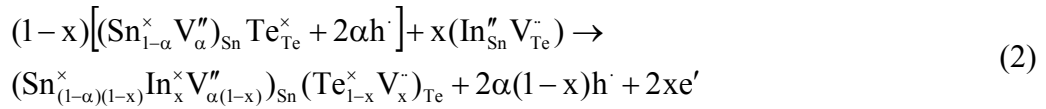
The introducing of a dopant can on diverse

superposition crystalloquasichemical cluster on the basic matrix. Crystalloquasichemical cluster is obtained by superposition crystallochemical structure of doped compound (in our case In^0) on the antistructure of basic matrix $SnTe$ ($V_{Sn}'' V_{Te}''$) [2]. For example, crystalloquasichemical representation of nonstoichiometric tin telluride with an excess of a tellurium in borders of homogeneity range is described by such equations:

influence on the defectively of crystalline lattice and change of carriers concentration. It depends on the mechanism of entering of an impurity in doped compound. In this article the two defect formation mechanisms are reviewed: the mechanism of substitution and mechanism of interstitial [3].

Crystalloquasichemical description of the defect formation at a substitution reaction given by the equations:



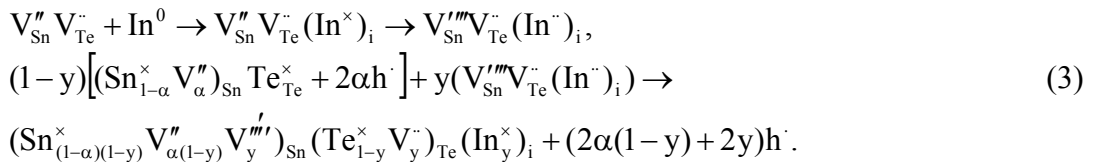


So, the localization of indium atoms in cationic vacancies is accompanied besides to decreasing it, both occurrence and increase of anionic vacancies concentration and defects of a new type – dopant substitutional atoms. Besides, by occupies of cationic vacancies, the atoms In reduce carrier concentrations, showing donor properties. Concentration dependences of defects, connected with substitution showed in a Fig. 2.

Compared experimental and calculational data, and using data of octahedral radiuses of Sn, Te, In atoms ($1,52 \cdot 10^{-8}$ cm, $1,64 \cdot 10^{-8}$ cm

and $1,65 \cdot 10^{-8}$ cm accordingly), can say that in the concentrations field $> 0,4$ at.% In the substitutional process is most probably. It confirms also by data of lattice constant changes, the decreasing of which one to assume, that the indium atoms taken the octahedral vacancies in sublattice of a tellurium. Uncoordination of concentration dependences character in the small doses border (up to $\sim 0,2$ at.% In) testifies about diverse mechanism of dissolution of an impurity in this compound.

In case of reactions of interstitial we have



As demonstrates crystalloquasichemical equation, the localization of indium atoms in tetrahedral vacancies of the close packing of tellurium atoms is accompanied by increase of

defects quantity of an acceptors type in Tin sublattice – tetra-ionised vacancies of Tin, which one results in sharp increase of carriers concentration (Fig. 3). The entering of In atoms

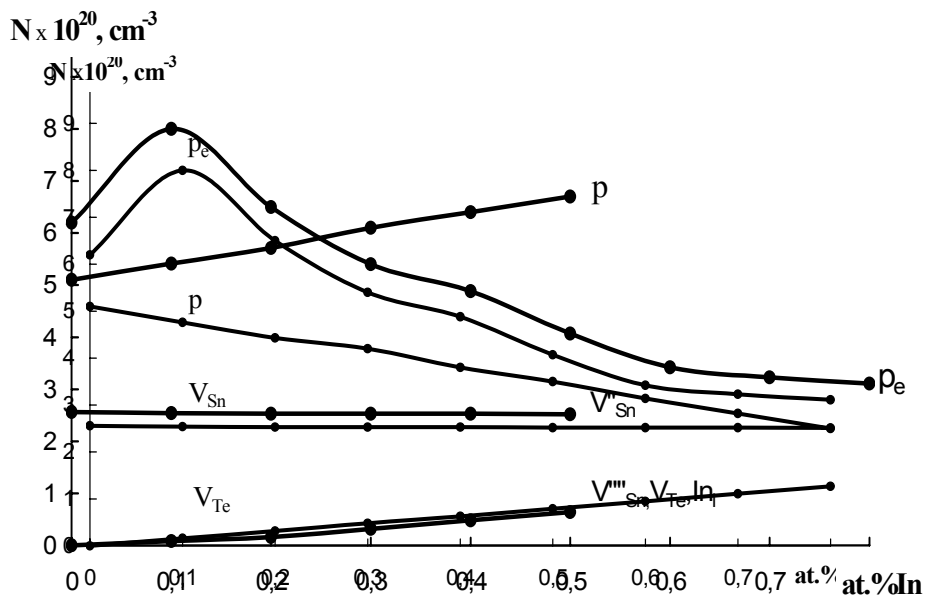


Fig. 2. Concentration dependence of current carriers and point defects versus dose of indium impurity at the substitutional mechanism.
Fig. 3. Concentration dependence of current carriers and point defects versus dose of indium impurity at the interstitial mechanism.

in tetrahedral vacancies is probable, as tetrahedral radius of it equals $1,27 \cdot 10^{-8}$ cm. the given process dominates on initial stages of the introducing of indium (up to $\sim 0,2$ at. % In), about what the sharp increasing of lattice parameter testifies.

On that time there is no unified thought concerning the mechanism of entering of indium in semiconductors like to $A^{IV}B^{VI}$ and its charge state. In the literature the probability of implementation of diverse charge states of indium atomic In^+ , In^{3+} are analysed [4]. Apparently, entering in SnTe matrix the atomic indium changes the charge state at the expense of availability in matrix as Sn^{2+} as Sn^{4+} , that

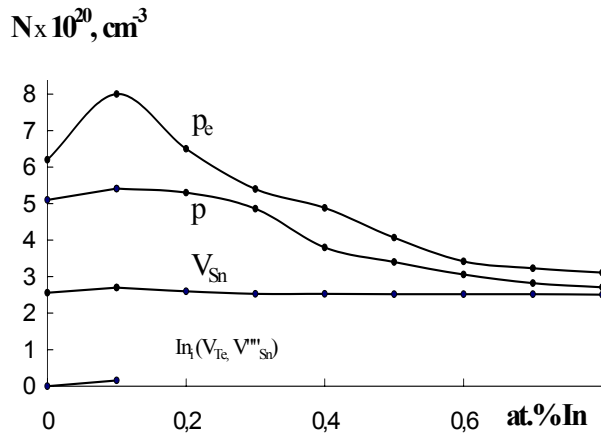


Fig. 4. Common picture of defect formation mechanisms in the system SnTe-In.

confirms by the data mossbauer spectroscopies. Besides, using the data of lattice parameter and octahedral radiuses of tin and tellurium, it is possible to say, that the sum of octahedral radiuses exceeds something interatomic interval ($3,18 \cdot 10^{-8}$ and $3,15 \cdot 10^{-8}$ cm). This divergence finds explanation if to suspect, that in the given connection exist double- and four-ionised atoms of tin. Analysing the concentration dependences on parties from 0,2 at.% up to 0,4 at.% In and compared its radiuses of atoms of interstitial and vacancies ($r_{In^{3+}}=1,27 \cdot 10^{-8}$ cm, $r_{V_{Sn}}=0,65 \cdot 10^{-8}$ cm), that both mechanism of defect formation are realised. Superposed these two mechanism, it is possible to receive a common picture of defect formation processes in tin monotelluride at doping its by the atomic indium (Fig. 4). So, it is possible to draw a conclusion, that indium is included in the basic

matrix SnTe on two mechanisms - mechanism of interstitial and mechanism of substitution, that is in nonstoichiometric SnTe it shows as acceptor (on initial stages of doping), and donors properties.

With the purpose of realization of more precise analysis of defect formation processes on the basis of the X-ray data the estimation of a maximum effective vacancy concentration in doped monocrystals SnTe was made. The calculations were made on the basis of sphere model for the help the formula for rock-salt structure

$$N_v = N_A \Delta V_{e.k.} / 4V_0$$

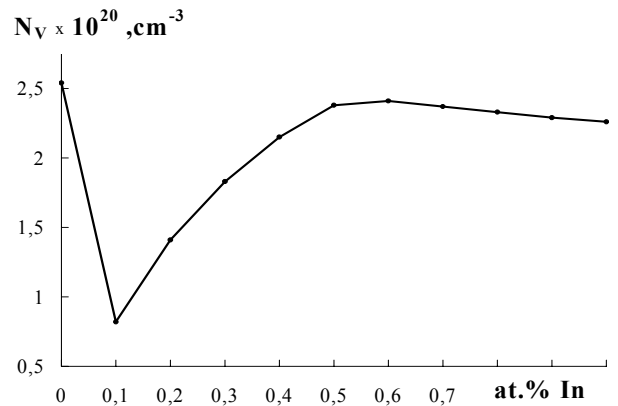


Fig. 5. Summary concentration of point defects calculated by the sphere model.

Where N_A – Avogadro constant;
 $\Delta V_{e.l.} = a^3 - a_1^3$ – change of elementary lattice volume;

$V_0 = 4/3 \pi r^3$ – volume of vacancy;

r – crystallochemical radius of vacancy.

As it is possible to see from Fig. 5 in the borders of small concentrations of an indium impurity the quantity of vacancies decreases sharply. So, it is possible to explain sharp increase of lattice parameter at reaction of interstitial both entering of indium atoms in tetrahedral vacancies and possible annihilation of anionic and cationic vacancies in crystals by volume diffusion.

Is detected a very good accordance between calculated and estimated data. As we see, proposed crystalloquasichemical model of defect formation processes usable to analyse of

the defective subsystem state of tin growth and doping.
monotelluride depending on conditions of

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Дефектоутворення в монотелуриді олова при окта- та тетраедричному розміщенні індію

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Розглянуто вплив домішки атомарного індію на процеси дефектоутворення в монотелуриді олова при різних механізмах утворення твердого розчину. Запропоновано кристаллохімічний опис даних процесів. Виявлено добру узгодженість між експериментальними та обрахованими за допомогою даного методу результатами. Побудовано концентраційні залежності носіїв струму і точкових дефектів в залежності від вмісту домішки індію.