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# Atomic defects and physical-chemical properties of PbTe-InTe solid solutions

D.M. Freik, V.M. Boychuk, L.I. Mezhylovsjka

Vasyl Stefanyk Precarpathian University, 57, Shevchenko str., 76000 Ivano-Frankivsk, Ukraine,  
E-mail: freik@pu.if.ua

**Abstract.** Crystal-quasichemical equations of probable mechanisms inherent to formation of solid solutions based on lead telluride of the n-type in PbTe-InTe system are offered. Shown is the possibility to satisfactorily explain experimental results by filling with indium atoms

$\text{In}^{+2} \leftrightarrow \text{In}_1^{+1}\text{In}_2^{+3}$  (up to 3 mol. % InTe) octahedral hollows (OH) of close-packed arrangement of tellurium atoms in PbTe crystal lattice. At the greater content of indium telluride, the allocation of both  $\text{In}^{+1}$  on OH, and  $\text{In}^{+3}$  on tetrahedral hollows (TH), accordingly, takes place.

**Keywords:** lead telluride, indium telluride, solid solution, atomic defects, crystal-quasichemical reaction.

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## 1. Introduction

Lead telluride is a basic material for device structures working in the infrared range of an optical spectrum, and also in various thermoelectric devices [1–3]. It crystallizes in the structure of NaCl type, the space group  $\text{Fm}\bar{3}\text{m}-\text{O}_h^5$  with the lattice parameter  $a = 6.452 \text{ \AA}$  and is melted congruently at 1190 K. The nature of chemical bonds is rather complicated here and corresponds to the mixed ionic-covalence-metallic type. The ionicity of lattice determines considerable (by the order of magnitude) divergence between static  $\epsilon_0$  and high-frequency dielectric permittivities [2]. For lead telluride the existence of bilateral field of homogeneity and diversion from a stoichiometrical composition is characteristic, which causes major values ( $10^{18}$ – $10^{20} \text{ cm}^{-3}$ ) of concentration of current carriers, and various conductances, too. Thus, the surplus of lead determines n-type of conductance, as tellurium – the p-type [3].

Now nature of atomic defects and their charge states both in lead telluride and solid solutions based on it has not been ascertained yet [2]. And there is no common opinion about the mechanism of forming the solid solutions in Pb-In-Te system [4, 5].

In this paper we offer a crystal-quasichemical approach suitable for the analysis of a defect subsystem and mechanisms of solid solution formation in PbTe-InTe system.

## 2. Experiment

The state diagram of PbTe-InTe system is related to an eutectic type (Fig. 1) [4]. The eutectic composition is near 75 mol. % of InTe, temperature of nonvariant equilibrium – 913 K [4]. The limiting miscibility InTe in PbTe has not ascertained ultimately and by the data of various authors lies within 7 up to 35 mol. % [4, 5].

The alloys were prepared by direct melting of high-clean components in evacuated at  $10^{-2} \text{ Pa}$  quartz ampoules at 1300 K according to procedure [4]. The melt was maintained during 10 hours with application of vibrating intermixing. The subsequent homogenising annealing carried out at 950 K by 210 h, and quenching – in ice water.

The phase composition, microhardness and electrical properties of alloys in all the considered range of existence of these solid solutions we explored.

The experimental data are submitted in Fig. 2. It is found, that up to 20 mol. % of InTe the alloys are homogeneous, thus the lattice parameter decreases (Fig. 2, curve 1). Both curves of concentration dependences of the microhardness (Fig. 2, curve 2) and thermo-e.m.f. coefficient (Fig. 2, curve 1) clearly pronounce two inflection points: in the vicinity of concentrations ~3 and 20 mol. % of InTe. Stationary values of the lattice parameter, thermo-e.m.f. coefficient and microhardness after 20 mol. % of InTe, as well as results of the phase

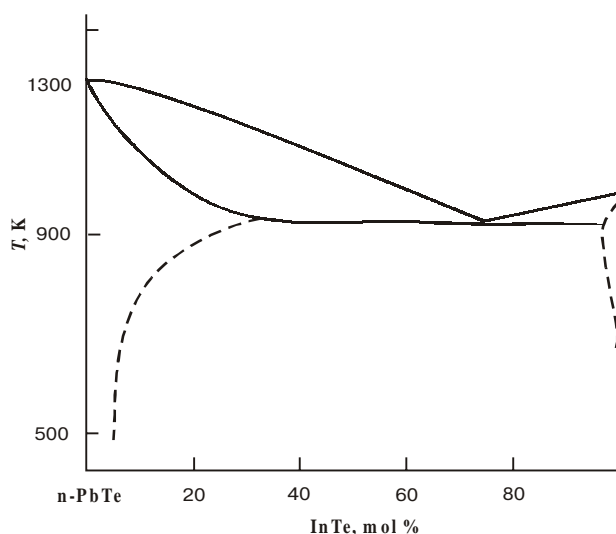


Fig. 1. The state diagram of PbTe-InTe system [4].

analysis confirm existence of biphase field, which is in accord with the data [4]. Diminution of the thermo-e.m.f. coefficient in alloys of composition 3–20 mol. % of InTe (Fig. 2, curve 1) is caused by propagation of the electron concentration (Fig. 2, curve 1). The observed decrease in the direct-current conductivity in the field of compositions up to 3 mol. % of InTe (Fig. 2, curve 2) can be explained by magnification of the contribution of an impurity dispersion, which causes decrease in of the mobility of current carriers (Fig. 2, curve 2). The stationary value of the direct-current conductivity for compositions 3 to 20 mol. % of InTe is supplied with the opposite change of the concentration and mobility of current carriers (Fig. 2b).

### 3. Crystal-quasichemical reaction of atomic defects

Existing models suitable for trying to explain properties of In impurity are possible to be conditionally separated into two groups [5]. In one of them indium is considered as an impurity centre with the basic state  $\text{In}^{+2}$ , and in another In is the multiply charged centre with states  $\text{In}^{+1}$  and  $\text{In}^{+3}$ . Therefore, from positions of valence rules, the chemical formula of indium telluride should be represented as  $\text{In}^{+2}\text{Te}^{-2} \leftrightarrow \text{In}_{\frac{1}{2}}^{+1}\text{In}_{\frac{1}{2}}^{+3}\text{Te}^{-2}$ . It is considered that

the Hubbard energy for electrons of In impurity is negative, therefore  $\text{In}^{+2}$  state is energy unprofitable.

For the analysis of the defect subsystem in PbTe-InTe solid solution, we have utilized the crystal-quasichemical approach [6].

This method is based on superposition of crystal-quasichemical clusters of the basic matrix and doping element, which is generated on the basis of anti-structure of the basic matrix. The anti-structure of lead telluride is

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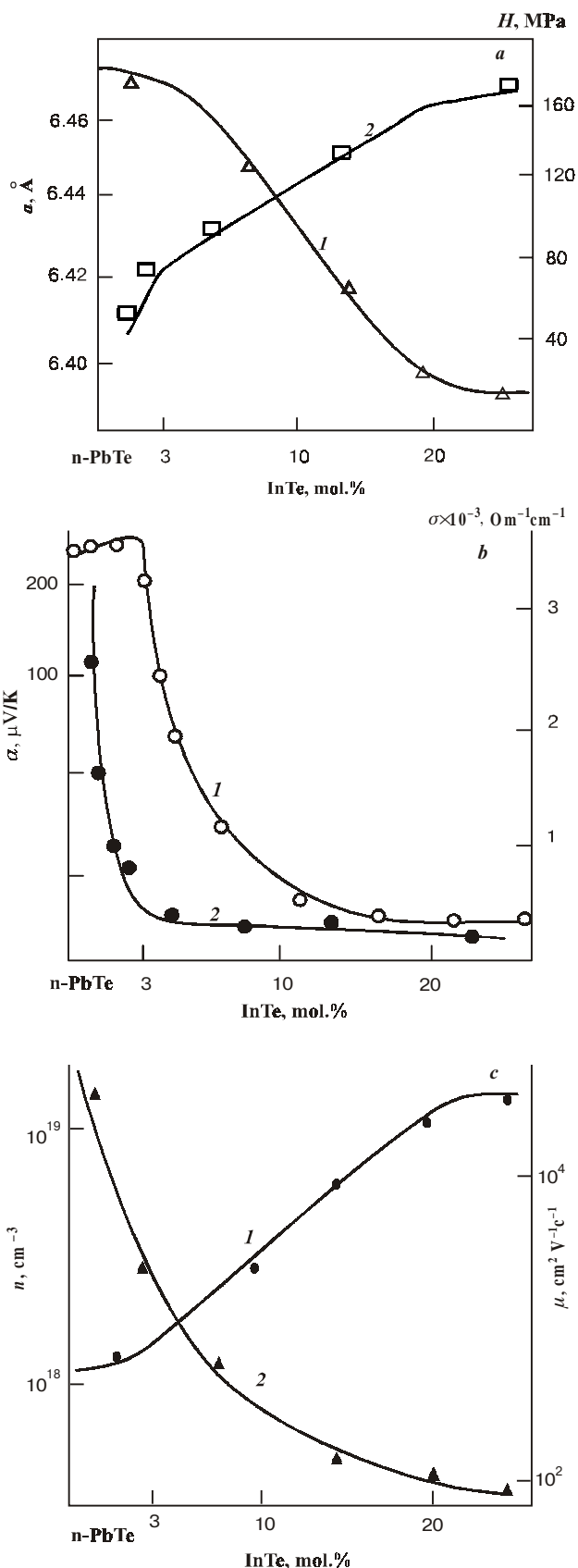
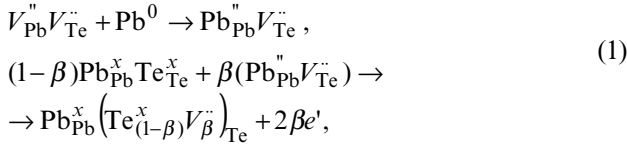


Fig. 2. Concentration dependences (a): parameter of a unit cell ( $a - 1$ ), microhardness ( $H - 2$ ); (b): coefficient of thermo-e.m.f. ( $\alpha - 1$ ), specific conductivity ( $\sigma - 2$ ); (c): concentrations ( $n - 1$ ) and mobility ( $\mu - 2$ ) of current carriers for PbTe-InTe system.

halenit  $V_{Pb}''V_{Te}''$ , where “'” and “''” are the negative and positive charges, respectively  $V_{Pb}''$  – doubly charged negative vacancy of lead, and  $V_{Te}''$  – doubly charged positive vacancy of tellurium.

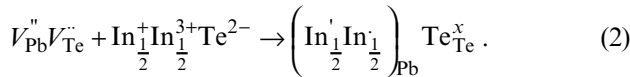
Crystal-quasichemical reaction of cluster formation in electronic material n-PbTe (with excess Pb) can be represented as follows:



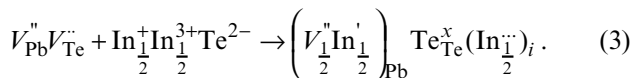
where  $Pb_{Pb}^x$ ,  $Te_{Te}^x$  – lead and tellurium in clusters of the crystal lattice, accordingly, “x” – neutral charge, “0” – zero charge,  $\beta$  – molecular ratio of a doping component,  $e'$  – electron concentration.

Thus, the electronic conduction of lead telluride is provided by vacancies in anionic  $V_{Te}''$  sublattice of the crystalline structure of lead telluride.

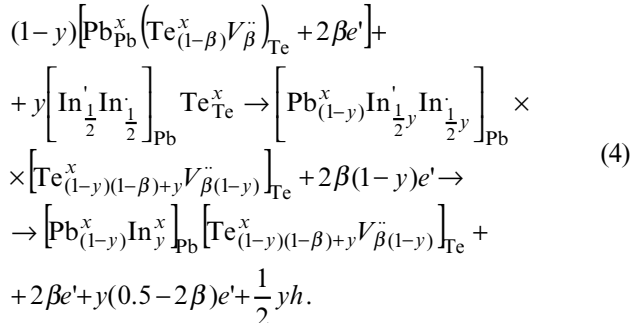
The doping of lead telluride by telluride of indium can be carried out by filling with lead vacancies the octahedral hollows of a close-packed arrangement of tellurium atoms in the crystal lattice (mechanism A). For this case crystal-quasichemical cluster of the doping impurity will be:



Besides, the solid solution formation can take place in such a way that  $In^+$  ions occupy the lead vacancies of the basic matrix ( $In^+ \rightarrow V_{Pb}''$ ), and triply charged  $In^{3+}$  ions are implanted in tetrahedral hollows of a close-packed arrangement of tellurium atoms of lead telluride crystal lattice ( $In^{3+} \rightarrow In_i^{3+}$ ), which are free (mechanism B):

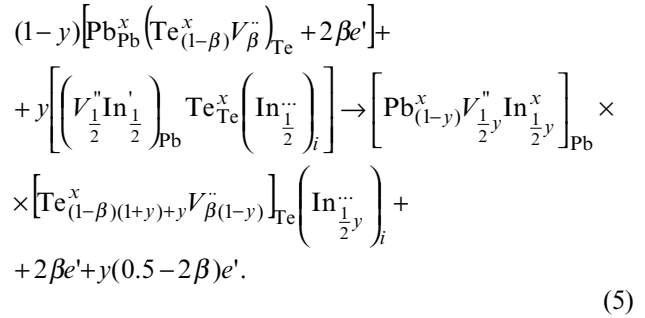


Let's consider a superposition of alloying clusters with the basic matrix of a n-type for various mechanisms of solid solution formation. The mechanism (A):



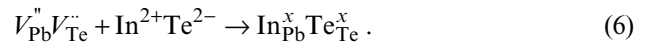
Thus, interaction of the doping cluster with the n-type material, in accord with this mechanism, for the decrease in vacancy number in the anionic sublattice implies an increase of majority carriers concentration. Here,  $(V_{\beta}'' )_{Te} > (V_{\beta(1-y)}'' )_{Te}$  is valid, and  $2\beta e' < 2\beta e' + y(0.5 - 2\beta)e'$  ( $y < 1$ ).

The mechanism (B):

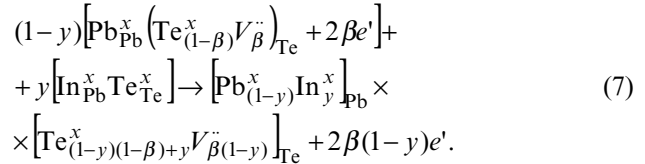


In this case, the solid solution formation leads to increase of the electron concentration  $(2\beta e' + y(0.5 - 2\beta)e' > 2\beta e'$ ,  $y < 1$ ), which is determined by redistribution of vacancies between both sublattices – cationic and anionic. Thus, intercalation of interstitial indium  $In_i^{3+}$  also takes place tetrahedral hollows in the close-packed arrangement of tellurium atoms of PbTe crystalline structure.

In the case of embodying the charged  $In^{+2}$  state in accord with the mechanism of filling the doping cluster, the reaction will accept the following look:

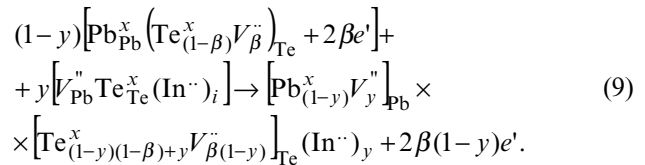
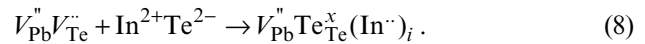


The solid solution formation will be carried out according to:



The decrease of the electron concentration  $(2\beta e' > 2\beta(1-y)e'$ ,  $y < 1$ ) due to defect redistribution in an anionic sublattice takes place.

Taking into account the mechanism of  $In^{+2}$  intercalation, the alloy cluster will be:



Similarly to results received in (7), it is seen that the electron concentration decreases due to defect redistribution between cationic and anionic sublattices of the basic matrix.

#### 4. Discussion

In accord with the above mentioned crystal-quasichemical equations (4) and (5) for solid solution formation in PbTe-InTe system, taking into account both the mechanism of

**Table 1. Electronic structure and elements radii of Pb, Te and In [7].**

Element	Pb	Te	In
$r, E$			
	$4f^{14}5d^{10}6s^26p^2$	$4d^{10}5s^25p^4$	$3d^{10}4s^24p^1$
atomic	1,81	1,42	2
covalent	1,47	1,36	1,44
ionic	1,26(+2)	2,11(-2)	1,30(+1), 1,27(+2), 0,92(+3)
octahedral	1,62	1,64	1,27
tetrahedral	1,46	1,34	–

filling (mechanism A (4)), and mechanism of intercalation (mechanism B (5)), doping of indium telluride develops the donor properties. To determine, which of these mechanisms plays a preferential role at the given InTe concentrations, it seems possible if being based on a comparison of experimental results (Fig. 2) as well as crystal-quasichemical parameters of separate atoms (Tab. 1) and crystal lattice (Tab. 1, 2) [7].

So, apparent from the experiment stationary values of current carriers concentration (Fig. 2, curve 1) and thermo-e.m.f. coefficient (Fig. 2, curve 1) in the range up to 3 mol.% of InTe confirm inappreciable donor activity of a doping impurity. It can be agree with (4) when embodying the mechanism of filling OH by indium in a state  $In^{+1}+In^{+3}$ . For concentration range 3 to 20 mol. % of InTe, the most probable mechanism of solid solution formation is filling the octahedral ( $In^{+1} > OH$ ) and tetrahedral hollows ( $In^{+3} > TH$ ) in close-packed arrangement of

**Table 2. Radii of tetrahedral ( $r_{TH}$ ) and octahedral ( $r_{OH}$ ) hollows for the close-packed arrangement of Pb and Te in various states of PbTe structure.**

Elements	$r_{TH}, E$	$r_{OH}, E$
Te (at.)	0.73	1.81
Te (cov.)	0.79	1.87
Te (2-) (ionic)	0.04	1.12
Pb (at.)	0.34	1.42
Pb (cov.)	0.68	1.76
Pb (+2) (ionic)	0.89	1.97

tellurium atoms of PbTe crystalline structure (5). As the vacancies in cationic and anionic sublattices are formed, and radius  $In^{+3}$  a little bit differs from radius of the tetrahedral hollow in tellurium sublattice (Tab. 1, 2) the diminution of the lattice parameter, and also increasing the electron concentration (Fig. 2, curve 1) takes place. The considerable change of the defect state in the crystal lattice cause a decrease of current carrier mobility (Fig. 2, curve 2) and increase of microhardness (Fig. 2, curve 2).

Two mechanisms of solid solution formation in accord with (7) and (9) are improbable, as they cause decreasing the majority current carrier concentration, which contradicts to the experiment (Fig. 2, curve 1).

## 5. Conclusions

1. The crystal-quasichemical mechanisms of solid solution formation in the system PbTe-InTe are offered.

2. It is ascertained, that the donor activity of doping impurity can be caused by two mechanisms, namely: filling the lead vacancies with indium atoms and simultaneous embodying both the mechanism of filling octahedral hollows with  $In^{+1}$ , and tetrahedral hollows with  $In^{+3}$  in the close-packed arrangement of tellurium atoms in PbTe crystalline structure.

3. Determined are concentration ranges of doping impurity, for which one of the mechanisms of solid solution formation prevails.

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