

Charge State of Indium and Point Defects in Indium-Doped Lead Telluride Crystals

D. M. Freik, V. M. Boichuk, and L. I. Mezhirovskaya

Physicochemical Institute, Stefanik University, Galitskaya ul. 201, Ivano-Frankovsk, 76000 Ukraine

e-mail: freik@pu.if.ua

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Abstract—Experimental data on the lattice parameter, thermoelectric power, and microhardness of PbTe(In) crystals and the conversion from *p*- to *n*-type with increasing indium content can be interpreted under the assumption that the indium in PbTe(In) has variable valence: $2\text{In}^{2+} \longleftrightarrow \text{In}^+ + \text{In}^{3+}$. A crystal-quasi-chemical model is proposed for defect formation in PbTe(In): the incorporation of In^+ into octahedral interstices and In^{3+} into tetrahedral interstices of the close packing of Te atoms, accompanied by In_2Te_3 precipitation.

INTRODUCTION

Lead telluride, PbTe, is a basic material for active elements operating in the infrared spectral region and also for thermoelectric converters [1–5]. PbTe crystallizes in the NaCl structure ($a = 6.461 \text{ \AA}$) [6] and has a complicated, ionic–covalent–metallic bonding configuration. The homogeneity range of PbTe involves both Te-enriched and Te-deficient compositions, with the highest Te content of 49.994–50.01 at % at 1048 K [2, 3]. The chemistry of native defects in PbTe depends on the cation-to-anion ratio. The native defects ensure a rather high carrier concentration (10^{18} to 10^{19} cm^{-3}) and play a key role in determining the conductivity type. Pb and Te vacancies are known to act as acceptors and donors, respectively [3].

Group III impurities, in particular Ga, In, and Tl, have a specific effect on the electronic spectrum of PbTe, producing deep and resonance states [7]. A feature common to these impurities is the stabilization (pinning) of the chemical potential at impurity levels. At the same time, the electronic properties of PbTe crystals doped with Group III elements depend strongly on the dopant. For example, thallium is a deep acceptor and produces resonance states within the valence band. Gallium creates impurity levels in the band gap and acts as a donor. The mechanism of indium accommodation and the charge state of this impurity in PbTe have not been fully investigated. Indium creates different states near the bottom of the conduction band and, accordingly, acts as a donor.

The objective of this work is to analyze the charge state of indium and models of point defects in PbTe(In) crystals.

PHYSICOCHEMICAL PROPERTIES OF PbTe–In ALLOYS

The PbTe–In phase diagram was studied by Lapitov *et al.* [8]. Published data on indium solubility in PbTe are contradictory. According to Batyushkova *et al.* [9], the solubility limit of In at 823 K is about 5 at %, whereas Belokon' *et al.* [6] hold that PbTe dissolves up to 20–25 at % In. As shown by precision measurements, the lattice parameter of PbTe(In) decreases with increasing indium content (Fig. 1). At $N_{\text{In}} = 3 \times 10^{19} \text{ cm}^{-3}$ (2 at % In), the conductivity of the material changes from *p*- to *n*-type (Fig. 2). The plots of microhardness H and thermoelectric power α versus indium content for stoichiometric PbTe (Fig. 3) show well-defined breaks at 1.5 and 5 at % In. With increasing indium content, H increases, whereas α decreases (Fig. 3).

Physicochemical studies of Pb-enriched PbTe–In alloys demonstrate that the thermoelectric power remains constant at indium contents of up to 0.75 at % and slightly decreases at 1 at % In. Further increase in indium content is accompanied by a rise in α and a reduction in H . An excess of tellurium increases the thermoelectric power, independent of N_{In} (Fig. 4, curve 1). The plot of microhardness versus Te content

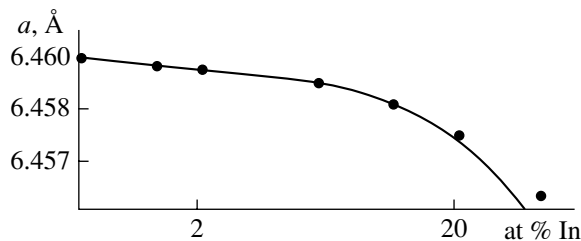


Fig. 1. Lattice parameter as a function of indium content for indium-doped lead telluride [6].

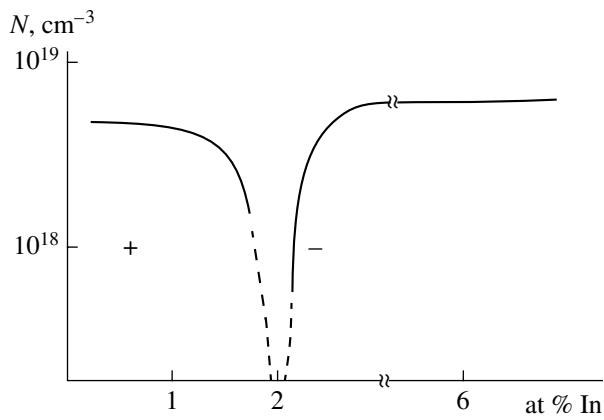


Fig. 2. 77-K carrier concentration in PbTe(In) as a function of indium content [6].

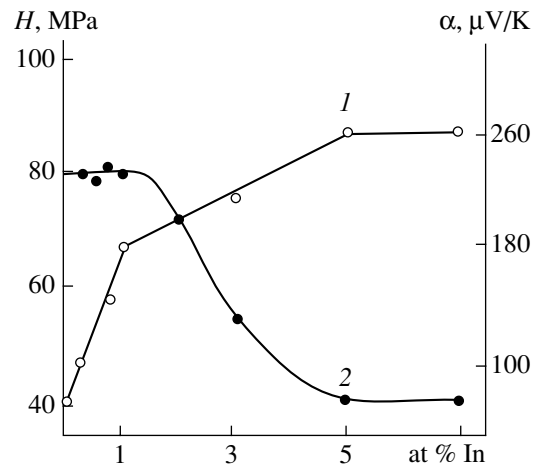


Fig. 3. Plots of (1) microhardness and (2) thermoelectric power vs. In content for PbTe(In) containing 50 at % Te [9].

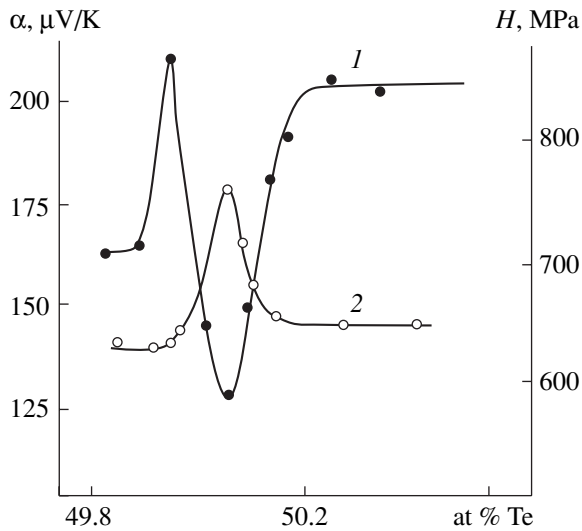


Fig. 4. Plots of (1) thermoelectric power and (2) microhardness vs. Te content for PbTe(In) containing 3 at % In [9].

at $N_{\text{In}} = \text{const}$ (Fig. 4, curve 2) shows a maximum at about 50 at % Te.

CHARGE STATE OF INDIUM IN PbTe(In)

The models used to interpret the behavior of In impurity in PbTe can be divided into two groups. In a number of models, indium is assumed to be mainly in the In^{2+} state. In the other group of models, the In^+ , In^{2+} , and In^{3+} states are allowed for. The In^{2+} state is energetically unfavorable since the Hubbard energy for the electrons of In impurity is negative and, hence, the charge state of In impurity changes through the transition of two electrons according to the scheme $2\text{In}^{2+} \longleftrightarrow \text{In}^+ + \text{In}^{3+}$ [10].

To identify the charge state of indium in PbTe, Drabkin *et al.* [10] used magnetic susceptibility measure-

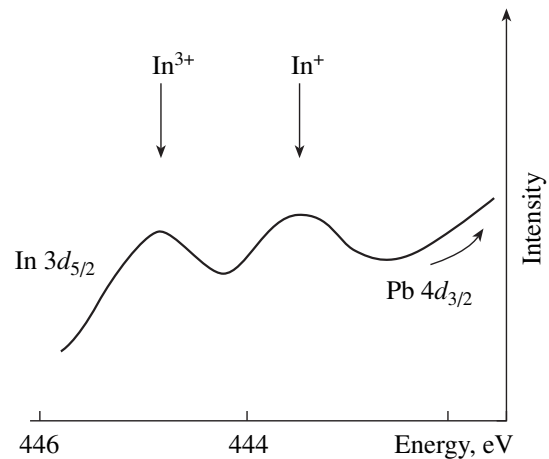


Fig. 5. X-ray photoelectron spectrum of $\text{Pb}_{0.99}\text{In}_{0.01}\text{Te}$ [10].

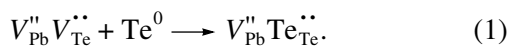
ments and x-ray photoelectron spectroscopy (XPS). Divalent indium ($5s^15p^2$ configuration) has one unpaired electron, whose spin would be expected to give rise to Langevin paramagnetism. Magnetic susceptibility measurements, however, show no indication of paramagnetism [10], suggesting that there is a mechanism of spin pairing in indium. In accordance with magnetic measurements, XPS results provide evidence that indium in PbTe crystals is present in two charge states: In^{3+} and In^+ (Fig. 5).

Comparison of the In valence-electron levels in PbTe with the energy levels of tellurium allows the valence state of the impurity to be assessed. Indium-doped PbTe crystals are *n*-type because the energy of the valence *s* and *p* electrons of In is higher than that of the valence *p* electrons of Te (Fig. 6) [11].

CRYSTAL-QUASI-CHEMICAL REACTIONS OF POINT-DEFECT FORMATION

Lead telluride crystallizes in the NaCl structure, which contains octahedrally and tetrahedrally coordinated atoms and octahedral and tetrahedral interstices (Fig. 7). The octahedral interstices are Te and Pb vacancies, and the tetrahedral interstices are unoccupied sites in the tetrahedral surrounding of Pb or Te (Fig. 7).

The crystal-chemical approach proposed by Lisnyak *et al.* [12] for analyzing defect formation processes deals with a superposition of a crystal-chemical cluster and an antistructure of the host phase. The antistructure of lead telluride is galenite, $V_{\text{Pb}}'' V_{\text{Te}}^{\bullet\bullet}$. In the presence of excess tellurium, the antistructure of stoichiometric PbTe forms a cluster with V_{Pb}'' :



Here, V_{Pb}'' and $V_{\text{Te}}^{\bullet\bullet}$ are negatively and positively

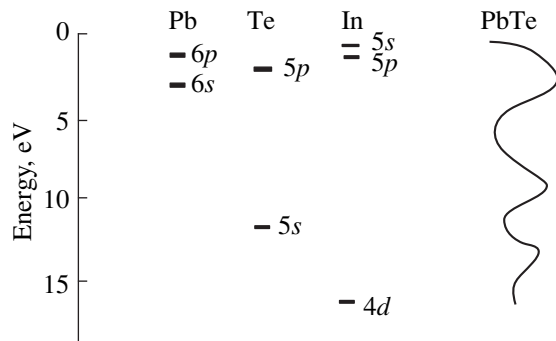


Fig. 6. Valence-electron spectra of Pb, Te, In, and PbTe [11].

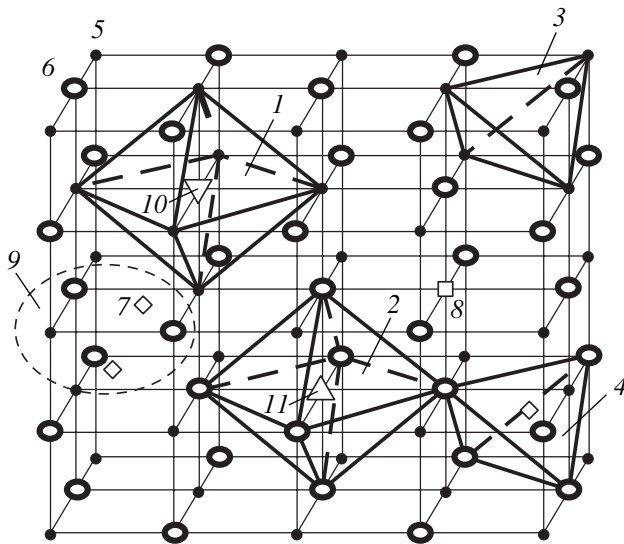
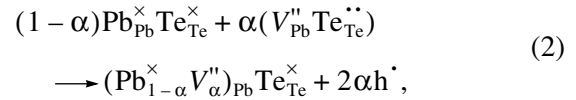


Fig. 7. Structure of imperfect PbTe crystals: (1, 2) octahedral interstices, (3, 4) tetrahedral interstices, (5) Pb, (6) Te, (7) trivalent indium in tetrahedral interstices, (8) univalent indium in an octahedral interstice, (9) In_2Te_3 phase, (10) Te vacancy, (11) Pb vacancy.

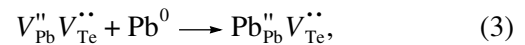
charged Pb and Te vacancies, respectively; Te_{Te} is a tellurium ion on a normal lattice site, and Te^0 is a neutral tellurium atom. A superposition of cluster (1) and the crystal-quasi-chemical formula of the host phase, $\text{Pb}_{\text{Pb}}^{\times} \text{Te}_{\text{Te}}^{\times}$, has the form



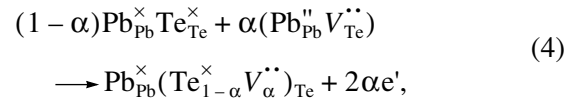
where α is the deviation from stoichiometry, h^{\cdot} is a hole, and $\text{Pb}_{\text{Pb}}^{\times}$ is a Pb ion on a normal lattice site.

It follows from Eq. (2) that the hole conduction in p -PbTe is due to negatively charged cation vacancies, $(V_{\alpha}'')_{\text{Pb}}$. In our approach, Pb vacancies (V_{Pb}'') are thought of as octahedral interstices in the cation environment of tellurium atoms (Fig. 7).

The crystal-quasi-chemical description of n -PbTe (Pb content in excess of the stoichiometric value) has the form



where, Pb^0 is a neutral Pb atom. A superposition of cluster (1) and the crystal-quasi-chemical formula of the host phase, $\text{Pb}_{\text{Pb}}^{\times} \text{Te}_{\text{Te}}^{\times}$, has the form

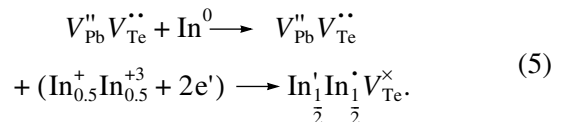


where e' is an electron.

It follows from Eq. (4) that an excess of Pb leads to the formation of additional tellurium vacancies, $(V_{\alpha}^{\bullet\bullet})_{\text{Te}}$, and increases the concentration of free electrons ($2\alpha e'$), which are responsible for the n -type conductivity of the material.

The In impurity in $\text{PbTe}\langle\text{In}\rangle$ crystals may occupy vacant Pb sites (mechanism A) or tetrahedral sites in the close packing of Te atoms (mechanism B) (Fig. 7).

1. Mechanism A (vacancy filling). A superposition of indium and the antistructure of the host phase yields the following cluster:



For p -type solid solutions, crystal-quasi-chemical equations have the form

$$(1-x)\{[\text{Pb}_{1-\alpha}^{\times}V_{\alpha}^{\prime\prime}]_{\text{Pb}}\text{Te}_{\text{Te}}^{\times} + 2\alpha h^{\cdot}\} \\ + x\left\{\text{In}_{\frac{1}{2}}^{\cdot}\text{In}_{\frac{1}{2}}^{\cdot}V_{\text{Te}}^{\times}\right\} \\ \rightarrow \left[\text{Pb}_{(1-\alpha)(1-x)}^{\times}V_{\alpha(1-x)}^{\prime\prime}\text{In}_{\frac{1}{2}x}^{\cdot}\text{In}_{\frac{1}{2}x}^{\cdot}\right]_{\text{Pb}} [\text{Te}_{1-x}^{\times}V_x^{\prime\prime}]_{\text{Te}} \\ + 2\alpha(1-x)h^{\cdot} + 2xe^{\prime}. \quad (6)$$

In this case, indium fills Pb vacancies in octahedral interstices of the close packing of Te atoms, thereby reducing the concentration of cation vacancies, $V_{\alpha(1-x)}^{\prime\prime} \rightarrow V_{\alpha}^{\prime\prime}$ ($\alpha(1-x) < \alpha$ since $x < 1$), and, hence, the hole concentration ($2\alpha(1-x)h^{\cdot}$) and leading to the generation of free electrons ($2xe^{\prime}$).

For n -PbTe, we have

$$(1-x)\{[\text{Pb}_{\text{Pb}}^{\times}[\text{Te}_{(1-\alpha)}^{\times}V_{\alpha}^{\prime\prime}]]_{\text{Te}} + 2\alpha e^{\prime}\} \\ + x\left\{\text{In}_{\frac{1}{2}}^{\cdot}\text{In}_{\frac{1}{2}}^{\cdot}V_{\text{Te}}^{\times}\right\} \\ \rightarrow \left[\text{Pb}_{(1-x)}^{\times}\text{In}_{\frac{1}{2}x}^{\cdot}\text{In}_{\frac{1}{2}x}^{\cdot}\right]_{\text{Pb}} [\text{Te}_{(1-\alpha)(1-x)}^{\times}V_{\alpha(1-x)+x}^{\prime\prime}]_{\text{Te}} \\ + 2\alpha(1-x)e^{\prime} + 2xe^{\prime}. \quad (7)$$

As in the case of Eq. (6), indium is incorporated into the Pb sublattice. According to Eq. (7), the incorporation of indium increases the concentrations of free electrons and anion vacancies ($\alpha < \alpha + x(1-\alpha)$), that is, the concentration of negative charge carriers.

2. Mechanism B (incorporation). By analogy with the above, we have

$$V_{\text{Pb}}^{\prime\prime}V_{\text{Te}}^{\prime\prime} + \text{In}^0 \\ \rightarrow V_{\text{Pb}}^{\prime\prime}V_{\text{Te}}^{\times}\left(\text{In}_{\frac{1}{2}}^{\cdot}\text{In}_{\frac{1}{2}}^{\cdot}\right)_i \rightarrow V_{\text{Pb}}^{\prime\prime}V_{\text{Te}}^{\times}(\text{In}^{\cdot\cdot})_i. \quad (8)$$

Defect formation in p -PbTe can be represented by the equation

$$(1-x)[(\text{Pb}_{1-\alpha}^{\times}V_{\alpha}^{\prime\prime})_{\text{Pb}}\text{Te}_{\text{Te}}^{\times} + 2\alpha h^{\cdot}] \\ + x[V_{\text{Pb}}^{\prime\prime}V_{\text{Te}}^{\times}(\text{In}^{\cdot\cdot})_i] \\ \rightarrow [\text{Pb}_{(1-\alpha)(1-x)}^{\times}V_{\alpha(1-x)+x}^{\prime\prime}]_{\text{Pb}} [\text{Te}_{1-x}^{\times}V_x^{\prime\prime}]_{\text{Te}}(\text{In}_x^{\cdot\cdot})_i \\ + 2\alpha(1-x)h^{\cdot} + 2xe^{\prime}. \quad (9)$$

Here, the redistribution of defects in the cation sublattice and the increase in the concentration of anion

vacancies also lead to a reduction in hole concentration and generation of free electrons.

In a similar manner, we have for n -PbTe

$$(1-x)[\text{Pb}_{\text{Pb}}^{\times}(\text{Te}_{1-\alpha}^{\times}V_{\alpha}^{\prime\prime})_{\text{Te}} + 2\alpha e^{\prime}] \\ + x[V_{\text{Pb}}^{\prime\prime}V_{\text{Te}}^{\times}(\text{In}^{\cdot\cdot})_i] \\ \rightarrow [\text{Pb}_{1-x}^{\times}V_x^{\prime\prime}]_{\text{Pb}} [\text{Te}_{(1-\alpha)(1-x)}^{\times}V_{\alpha(1-x)+x}^{\prime\prime}]_{\text{Te}}(\text{In}_x^{\cdot\cdot})_i \\ + 2\alpha(1-x)e^{\prime} + 2xe^{\prime}. \quad (10)$$

Thus, indium incorporated in tetrahedral interstices of p - or n -type PbTe acts as a donor, increasing the concentration of free electrons and, according to the Le Chatelier principle, the concentrations of both cation and anion vacancies.

DISCUSSION

It follows from the above analysis of the main mechanisms underlying the incorporation of indium in octahedral and tetrahedral interstices in the close packing of Te atoms, represented by Eqs. (6), (7), (9), and (10), that In impurity in PbTe behaves as an effective donor. One can ascertain which mechanism prevails by analyzing the crystal-chemical parameters of the constituent atoms and PbTe lattice (Tables 1, 2) and experimental property-composition data (Fig. 1-4).

In particular, the reduction in lattice parameter upon indium doping of PbTe (Fig. 1) can be accounted for under the assumption that indium predominantly occupies vacant Pb sites (mechanism A), since the average of the ionic radii of In^+ and In^{3+} is $r_{\text{In}} = 1.09 \text{ \AA}$, which is considerably smaller than the ionic radius of Pb, $r_{\text{Pb}} = 1.26 \text{ \AA}$ (Table 1). In addition, the relationships between the octahedral radii of Pb (1.62 \AA) and In (1.27 \AA) and their covalent radii (1.47 and 1.44 \AA , respectively) (Table 1) also suggest that indium doping must reduce the lattice parameter of PbTe.

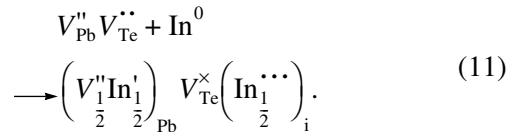
Mechanism B (incorporation of indium into tetrahedral interstices of the close packing of Te atoms in the structure of PbTe) appears unlikely because the radius of the tetrahedral interstices is very small (0.04 – 0.73 \AA , Table 2), and the incorporation of indium in any state ($r_{\text{In}} = 0.92$ – 2 \AA , Table 1) would, no doubt, increase the lattice parameter of PbTe, at variance with experimental results (Fig. 1).

Since the coexistence of In atoms in different valence states, $2\text{In}^{2+} \longleftrightarrow \text{In}^+ + \text{In}^{3+}$, in the cation sublattice, as represented by Eqs. (6) and (7), is not fully substantiated, we propose a third model of defect formation in which In^+ sits in cation sites, and In^{3+} sits in tet-

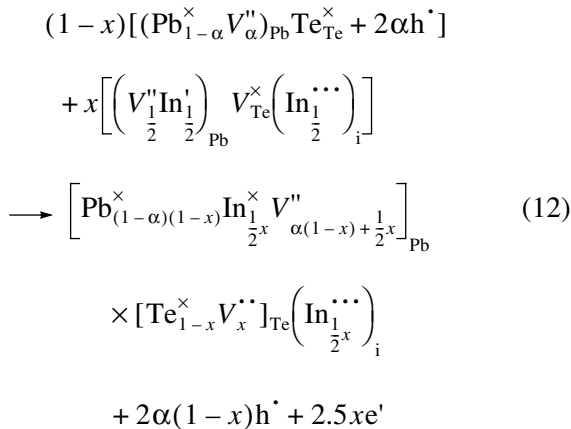
Table 1. Electronic configurations and radii (Å) of Pb, Te, and In [13]

Element	Pb	Te	In
Configuration	$4f^{14}5d^{10}6s^26p^2$	$4d^{10}5s^25p^4$	$3d^{10}4s^24p^1$
r_{atomic}	1.81	1.42	2
r_{covalent}	1.47	1.36	1.44
r_{ionic}	1.26 (2+)	2.11 (2-)	1.30 (+), 1.27 (2+), 0.92 (3+)
$r_{\text{octahedral}}$	1.62	1.64	1.27
$r_{\text{tetrahedral}}$	1.46	1.34	–

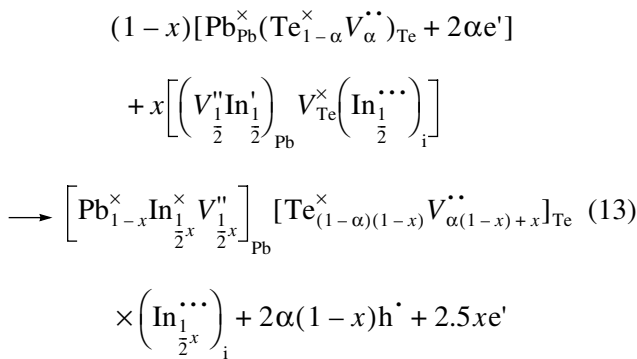
rahedral interstices of the close packing of Te atoms (mechanism C). The doping cluster then has the form



In this model, the crystal-quasi-chemical equations of defect formation have the form



for *p*-type PbTe(In) and



for *n*-type PbTe(In).

Thus, according to Eqs. (12) and (13) the In dopant also behaves as an effective donor. At the same time, even though $r_{\text{In}^{3+}} = 0.92 \text{ \AA}$ (Table 1), the incorporation

of indium into tetrahedral interstices must increase the lattice parameter, which is also at variance with experimental data (Fig. 1). In view of these inconsistencies, and taking into account the report by Belokon' *et al.* [6] that Czochralski-grown PbTe(In) single crystals may contain crystalline In₂Te₃ inclusions, we assume that In³⁺ interstitials, when present in considerable concentrations, tend to form an In₂Te₃ phase. Since the lattice parameter of cubic In₂Te₃ ($a = 6.16 \text{ \AA}$) is close to that of PbTe, small amounts of In₂Te₃ impurity are difficult to identify.

Thus, we are led to conclude that the dominant mechanism of In accommodation in PbTe crystals is the incorporation of In⁺ into the cation sublattice and In₂Te₃ precipitation. Owing to the formation of additional anion vacancies, as represented by Eqs. (12) and (13), indium acts as a donor, leading to a reduction in hole concentration, conversion from *p*- to *n*-type, and increase in electron concentration (Fig. 2). The reduction in the thermoelectric power of *n*-type PbTe(In) with increasing indium content (Fig. 3, curve 2) is due to the increase in the concentration of majority carriers, and the increase in its microhardness (Fig. 3, curve 1) is associated with the rise in lattice strain upon the incorporation of indium in vacant Pb sites.

The reduced microhardness of nonstoichiometric PbTe(In) crystals (Fig. 4, curve 2) is due to the elimination of cation or anion vacancies [Eqs. (2) and (4)] in the presence of excess Pb or Te, respectively, and the

Table 2. Radii of tetrahedral and octahedral interstices for close packing of Pb and Te in different states (PbTe structure)

Element	$r_{\text{tetrahedral}}, \text{ \AA}$	$r_{\text{octahedral}}, \text{ \AA}$
Te (atomic)	0.73	1.81
Te (covalent)	0.79	1.87
Te ²⁻	0.04	1.12
Pb (atomic)	0.34	1.42
Pb (covalent)	0.68	1.76
Pb ²⁺	0.89	1.97

associated reduction in lattice strain. As follows from Eq. (2), increasing the tellurium content in excess of the stoichiometric value at a constant indium content increases the concentration of cation vacancies and reduces the electron concentration, which is responsible for the observed increase in thermoelectric power (Fig. 4, curve 1). A more complicated situation occurs in Pb-enriched PbTe<In> crystals, where the variation in the concentration of majority carriers depends on the relationship between the Pb excess and In content.

CONCLUSIONS

Crystal-quasi-chemical models were proposed for defect formation in *n*- and *p*-type PbTe<In> crystals.

The indium in PbTe<In> was shown to have variable valence: $2\text{In}^{2+} \longleftrightarrow \text{In}^+ + \text{In}^{3+}$.

The dominant defect species in PbTe<In> crystals are In^+ in Pb sites and In^{3+} in tetrahedral interstices of the close packing of Te atoms.

At appreciable doping levels (above 1.5 at % In), In^{3+} interstitials tend to form cubic In_2Te_3 inclusions.

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