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Crystallochemistry of defects in lead telluride films

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Abstract. The crystallochemical model of vapor-phase epitaxy of the lead telluride films has been proposed with the supposition about the simultaneous formation of singly charged, doubly charged and electroneutral Frenkel defects in the cationic sublattice. It has been shown that in spite of the large concentration of partly compensated doubly charged defects the singly charged Frenkel pairs Pb_i^+ and V_{Pb}^- also play an essential role in change carrier concentration in PbTe films. The results of numerical calculation agree with the available experimental data of the dependence of charge carrier's concentration in films upon the partial pressure of tellurium vapor and the deposition's temperature in the hot-wall method.

Keywords: crystallochemistry, defects, films, lead telluride.

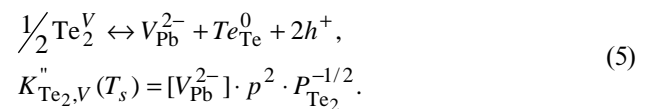
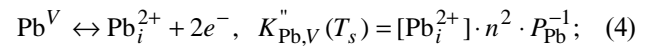
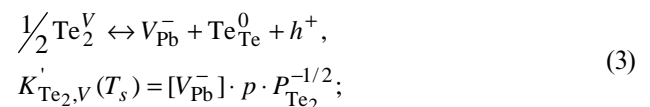
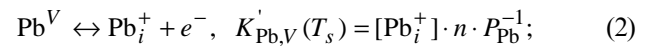
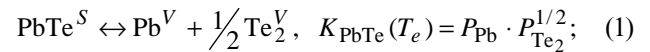
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1. It is known that it is possible to control the electric properties (i.e. conduction type and charge carrier concentration) of lead chalcogenides by varying their composition within the homogeneity region. However, there is no agreement in the literature concerning the predominant type of intrinsic defects in $A^{IV}B^{VI}$ and their charge state. For instance, based on analysis of the state diagrams and processes of annealing of lead telluride, the authors of [3] assumed the existence of singly charged acceptors V_{Pb}^- . Conclusions about the predominance of disordering in metal sublattice with formation of singly charge defects Pb_i^+ and V_{Pb}^- , regardless of enrichment by lead or chalcogenide, are drawn in [4]. There are also various opinions concerning the charge state of interstitial lead [5]. While in [6] it is assumed to be the doubly ionized donor (Pb_i^{2+}), in [3] it is considered as singly ionized Pb_i^+ . There have been attempts to explain the experimental dependence of electrical parameters of PbTe thin films on growth conditions by formation of singly charged interstitial atoms Pb_i^+ and doubly charged vacancies V_{Pb}^{2-} . In calculations of energy spectrum of atomic defects, their electrical activity is explained within the model assuming doubly charged metal V_{Pb}^{2-} and chalcogen V_{Te}^{2+} vacancies [5]. In [8] it has been shown that at low temperatures and high chalcogen vapour pressure, PbTe crystals have significant number of neutral intrinsic point defects along with singly ionized defects.

2. For the first time we introduce the model of metal sublattice disordering in PbTe thin films according to Frenkel mechanism with simultaneous formation of singly and doubly charged, as well as neutral defects: inter-

stitial lead atoms Pb_i^+ , Pb_i^{2+} , Pb_i^0 and lead vacancies V_{Pb}^- , V_{Pb}^{2-} , V_{Pb}^0 .

The equilibrium of «bulk weight – vapour» and «vapour – condensate» systems in the process of film growth from the vapour phase by the hot-wall method can be described by the following system of quasi-chemical reactions [10]:



Here equation (1) determines the equilibrium of «bulk weight – vapour» system in the process of PbTe decomposition in the evaporator at temperature T_e . Reactions (2)–(5) determine the equilibrium in the system «vapour – condensate» that is responsible for the intrinsic atomic defects at precipitation (substrate) temperature T_s .

The intrinsic conductivity and ionization of Frenkel defects are described by equations (6) and (7)–(12), respectively:

$$\langle 0 \rangle = e^- + h^+, \quad K_i(T_s) = n \cdot p; \quad (6)$$

$$\langle 0 \rangle = V_{Pb}^- + Pb_i^+, \quad K'_F(T_s) = [V_{Pb}^-][Pb_i^+]; \quad (7)$$

$$\langle 0 \rangle = V_{Pb}^{2-} + Pb_i^{2+}, \quad K''_F(T_s) = [V_{Pb}^{2-}][Pb_i^{2+}]; \quad (8)$$

$$\langle 0 \rangle = V_{Pb}^- + Pb_i^{2+} + e^-, \quad K_F^{(e)}(T_s) = [V_{Pb}^-][Pb_i^{2+}]n; \quad (9)$$

$$\langle 0 \rangle = V_{Pb}^{2-} + Pb_i^+ + h^+, \quad K_F^{(h)}(T_s) = [V_{Pb}^{2-}][Pb_i^+]p; \quad (10)$$

$$Pb_i^0 \leftrightarrow Pb_i^+ + e^-, \quad K_a(T_s) = [Pb_i^+]/[Pb_i^0]; \quad (11)$$

$$V_{Pb}^0 \leftrightarrow V_{Pb}^- + h^+, \quad K_b(T_s) = [V_{Pb}^-]p/[V_{Pb}^0]; \quad (12)$$

$$Pb_i^0 \leftrightarrow Pb_i^{2+} + 2e^-, \quad K'_a(T_s) = [Pb_i^{2+}]n^2/[Pb_i^0]; \quad (13)$$

$$V_{Pb}^0 \leftrightarrow V_{Pb}^{2-} + 2h^+, \quad K'_b(T_s) = [V_{Pb}^{2-}]p^2/[V_{Pb}^0]. \quad (14)$$

The general electroneutrality condition is:

$$p + [Pb_i^+] + 2[Pb_i^{2+}] = n + [V_{Pb}^-] + 2[V_{Pb}^{2-}]. \quad (15)$$

From (1)–(15) we obtain the equation determining the charge carriers concentration (n) in terms of quasi-chemical reaction constants K and P_{Te_2} :

$$An^4 + Bn^3 - Cn - D = 0. \quad (16)$$

Here

$$A = 2K''_{Te_2,V} K'_F \cdot P_{Te_2}^{1/2} \cdot (K_{PbTe} K'_{Pb,V} K'_{Te_2,V} K_i)^{-1};$$

$$B = 1 + K'_F \cdot P_{Te_2}^{1/2} \cdot (K_{PbTe} K'_{Pb,V})^{-1};$$

$$C = K_i + K_{PbTe} K'_{Pb,V} \cdot P_{Te_2}^{-1/2};$$

$$D = 2K_{PbTe} K''_{Pb,V} \cdot P_{Te_2}^{-1/2}.$$

The charge carrier concentration is determined experimentally by Hall effect:

$$n_H = n - p = n - K_i \cdot n^{-1}. \quad (17)$$

Within the suggested model, it is also possible to determine the concentrations of charged and electroneutral defects:

$$[Pb_i^+] = K_{PbTe} K'_{Pb,V} n^{-1} P_{Te_2}^{-1/2};$$

$$[Pb_i^{2+}] = K_{PbTe} K''_{Pb,V} n^{-2} P_{Te_2}^{-1/2};$$

$$[V_{Pb}^-] = K'_F \cdot n \cdot P_{Te_2}^{1/2} (K_{PbTe} K'_{Pb,V})^{-1}; \quad (18)$$

$$[V_{Pb}^{2-}] = K''_{Te_2,V} K'_F \cdot n^2 \cdot P_{Te_2}^{1/2} (K_{PbTe} K'_{Pb,V} K'_{Te_2,V} K_i)^{-1};$$

$$[Pb_i^0] = K_{PbTe} K'_{Pb,V} K_a^{-1} P_{Te_2}^{-1/2};$$

$$[V_{Pb}^0] = K'_F K_i P_{Te_2}^{1/2} (K_{PbTe} K'_{Pb,V} K_b)^{-1}.$$

3. The intrinsic conductivity constant K_i in equation (6) was determined from the temperature dependencies of the band-gap $E_g(T)$ and effective mass $m(T)$ [11]:

$$K_i(T_s) = N_c \cdot N_v \cdot e^{-E_g/kT}, \quad (19)$$

$$N_c = N_v = 2(mkT/2\pi\hbar^2)^{3/2},$$

$$\begin{cases} m(T) = g_c^{2/3} K^{1/3} \cdot 0,048 \cdot m_0 \sqrt{T/300}, \\ g_c = 4, K = m_{\parallel}/m_{\perp} = 9 (T \geq 300K), \end{cases} \quad (20)$$

$$E_g(T) = 0,217 + 4,5 \cdot 10^{-4} (T - 77)(\text{eV}), \\ (T \geq 77K).$$

Here, m_0 is the free electron mass, and K is the anisotropy constant of effective mass of electrons in conduction band and light holes in valence band.

K'_F was determined from equilibrium condition:

$$K'_F = K_{PbTe}(T_s) K'_{Pb,V}(T_s) K'_{Te_2,V}(T_s) K_i^{-1}(T_s). \quad (21)$$

Assuming that in the studied pressure range vapour can be treated as ideal gas, for the quasi-equilibrium state of «vapour–condensate» system we get:

$$K_{PbTe}(T_s) = K_{PbTe}(T_e) \cdot \left(\frac{T_s}{T_e} \right)^{3/2}.$$

Other reaction constants used in this paper are listed in the Table; they were taken from previous results for PbTe crystals [2, 3].

4. Experimental and theoretical results of dependency of charge carrier and defect concentration in PbTe films on technological factors (i.e. partial Te_2 vapour pressure P_{Te_2} and substrate temperature T_s) in the hot-wall method are presented in Fig. 1, 2. It is clear (Fig. 1) that the increase in Te vapour pressure in precipitation region and increase in substrate temperature lead to the initial decrease in electron concentration. At some values T_s^* and $P_{Te_2}^*$, the inversion of conductivity type from n to p oc-

Table. Equilibrium constants $K = K_0 \exp(-\Delta H/kT)$ of the quasi-chemical reactions.

Constants	K_0	$\Delta H, \text{eV}$
$K_{PbTe}, \text{Pa}^{3/2}$	$1,4 \cdot 10^{18}$	3.51
$K'_{Pb,V}, \text{cm}^{-6} \text{Pa}^{-1}$	$5,5 \cdot 10^{30}$	-1.01
$K'_{Te_2,V}, \text{cm}^{-6} \text{Pa}^{-1/2}$	$1,2 \cdot 10^{38}$	0.25
$K''_{Pb,V}, \text{cm}^{-9} \text{Pa}^{-1}$	$1,2 \cdot 10^{51}$	-0.87
$K''_{Te_2,V}, \text{cm}^{-9} \text{Pa}^{-1/2}$	$1,5 \cdot 10^{59}$	0.39
K_a, K_b, cm^{-3}	$6,5 \cdot 10^{20}$	0.14

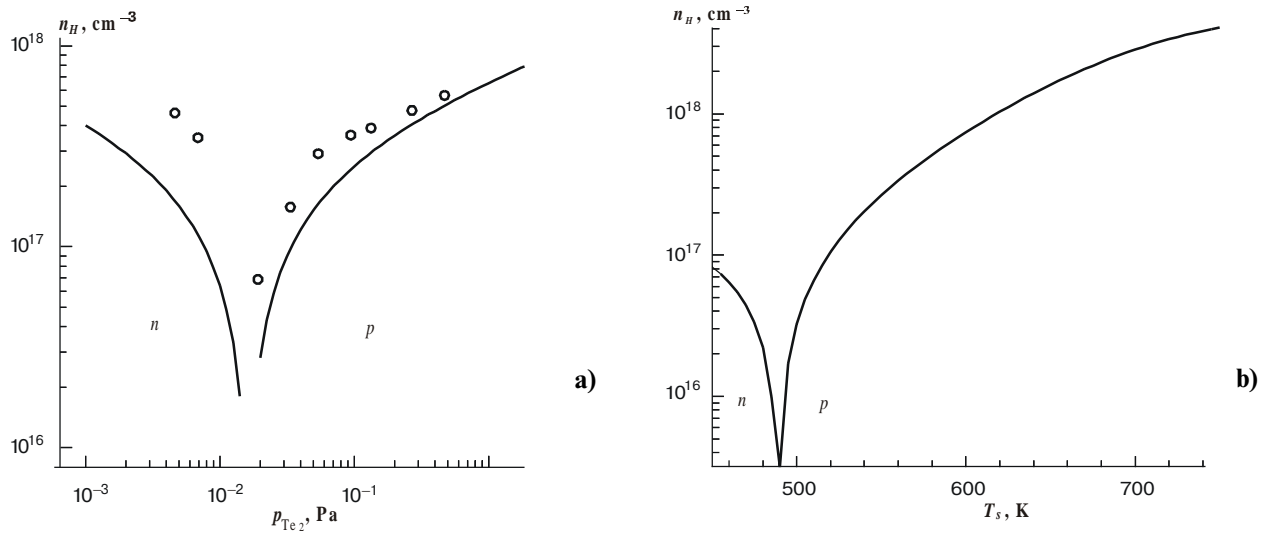


Fig. 1. Dependence of carrier concentration in PbTe films on:

(a) – the partial pressure of tellurim vapour ($T_s = 653\text{K}$, $T_e = 833\text{K}$) [12];

(b) – the substrate temperature ($P_{\text{Te}_2} = 1.65 \cdot 10^{-2} \text{Pa}$, $T_e = 720\text{K}$); the substrates are splinters of (111) BaF_2 ; the solid lines are calculated curves according to (16), (17).

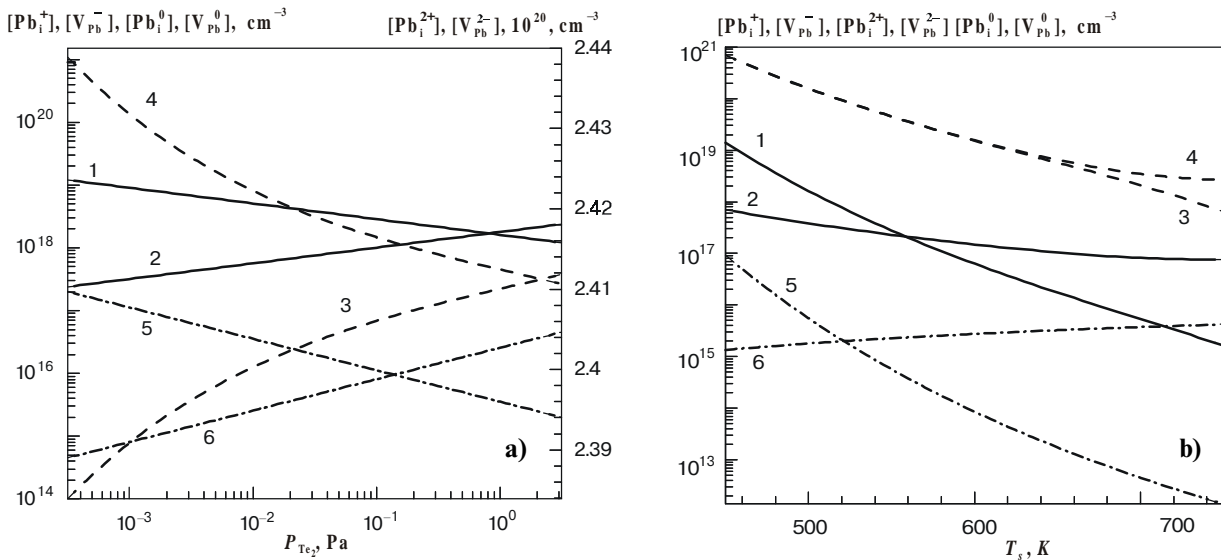


Fig. 2. Dependence of calculated concentration of defects according to (18) in PbTe films on:

(a) – the partial pressure of tellurim vapour ($T_s = 653\text{K}$, $T_e = 833\text{K}$);

(b) – the substrate temperature ($P_{\text{Te}_2} = 1.65 \cdot 10^{-2} \text{Pa}$, $T_e = 720\text{K}$).

The solid lines are singly charged defects $[\text{Pb}_i^+]$ (1) and $[\text{V}_{\text{Pb}}^-]$ (2), the dotted lines are doubly charged defects $[\text{Pb}_i^{2+}]$ (3) and $[\text{V}_{\text{Pb}}^{2-}]$ (4), the stroke-dotted lines are the electroneutral defects $[\text{Pb}_i^0]$ (5) and $[\text{V}_{\text{Pb}}^0]$ (6).

curs, followed by the further increase in hole concentration. It is worth mentioning that this change in charge carrier concentration (Fig. 1) is accompanied by the change of concentration of vacancies and interstitial lead atoms (Fig. 2). With the increase in T_s and P_{Te_2} , concentration of singly charged lead vacancies increases (Fig. 2, curve 1), and the concentration of singly ionized interstitial lead atoms decreases (Fig. 2, curve 2).

Doubly charged defects appear to be strongly compensated. According to our calculation (Fig. 2, curves 3, 4), their concentration is rather high and amounts to $\sim 10^{20} \text{ cm}^{-3}$ at $T_s = 653 \text{ K}$. This is two orders of magnitude higher than the concentration of singly ionized defects ($\sim 10^{18} \text{ cm}^{-3}$, Fig. 2), which is in turn exceeds the concentration of neutral defects (Fig. 2, curves 5, 6). This is in full agreement with our assumption about the predominance of the multiply charged vacancies and interstitial atoms that can be in different charge states in the presence of sufficiently shallow acceptor and donor levels [13]. Due to strong but incomplete compensation of the doubly charged defects (Fig. 2, curves 3,4), singly charged defects play comparably important role in changing charge carrier concentration in PbTe films.

Thus, the crystal-chemical calculation of equilibrium of intrinsic atomic defects in cation sublattice of PbTe films shows that the assumption of simultaneous existence of singly and doubly charged defects is most reasonable and is in agreement with the experimental data.

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