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Crystallochemistry of own atomic defects and thermodynam n-p-transition in the crystals of PbSe

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We examined the *n-p*-transition in the crystals of *PbSe* at the twotemperature anneal. The experimental result are explained by the creation of own atomic defects: interstitial atoms of lead (Pb_i^+), and vacancies of lead (V_{Pb}^-). The received analytical expressions describe the *n-p*-transition and also a dependence of concentration of charge carries on the temperature of anneal and partial pressure of the vapors of selenium. The technological conditions of formation the *PbSe* crystals with electric properties set before hand are determined.

Keywords: crystals *PbSe*, defects, balance constant, *n-p*-transition, anneal.

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I. Introduction

The *PbSe* are prospective materials for thermoelectricity and infrared technics [1,2]. The efficiency off using is determined by the opportunitics of receiving them with the properties set before hand. The own atomic defects connected with nonstoichiometry are fixed to influence greatly the electric parameters of $A^{IV}B^{VI}$ compounds [3].

The *PbSe* has a big area of homogeneity, which can be displace at the side of metal as well as at the side of chalcogen. For example, for rhe teemperatures 1073-1173 K the compound *PbSe* exists at the interval 49.8 – 50.05 at.% Se [4]. The superstoichiometry atoms of lead are fixed to locate in the interstice (Pb_i) and caausee the electron conduction, and the superstoichiometry atoms of selenium are responsible for the creation of vacancies in the sublattice of the metal (V_{Pb}) and condition the hole conduction.

The character and magnitude of nonstoichiometry can be changed by the twotemperature anneal of the $A^{IV}B^{VI}$ crystals in the vapors of chalcogen or metal, and so the type of conduction and concentration of charge carriers. Earlier in the works [6-8] such experiments for the crrystals of *PbTe* were carried out and there was made an extimation of the balance constants of formations defects, which were made more exast later [4]. At the same time the technological conditions of n-p-transition realizations in the *PbSe* crystals are not created up, which is important for the practice. There wasn't found expression which would give the possibility to describe analytically the dependence of the defects concentration and, accordingly, the berriers of the charge carriers on the conditions of annealing.

II. Experimental procedure and results

The *PbSe* crystals synthesized by the fusion of *Pb* and *Se* with the concentration of impurities not more than 10^{-4} % in vacuum quartz ampules. Anneal of this crystals in the vapors of selenium was conducted with the method of two temperatures [6]. To one end of the quartz ampule fused selenium was placed, to another

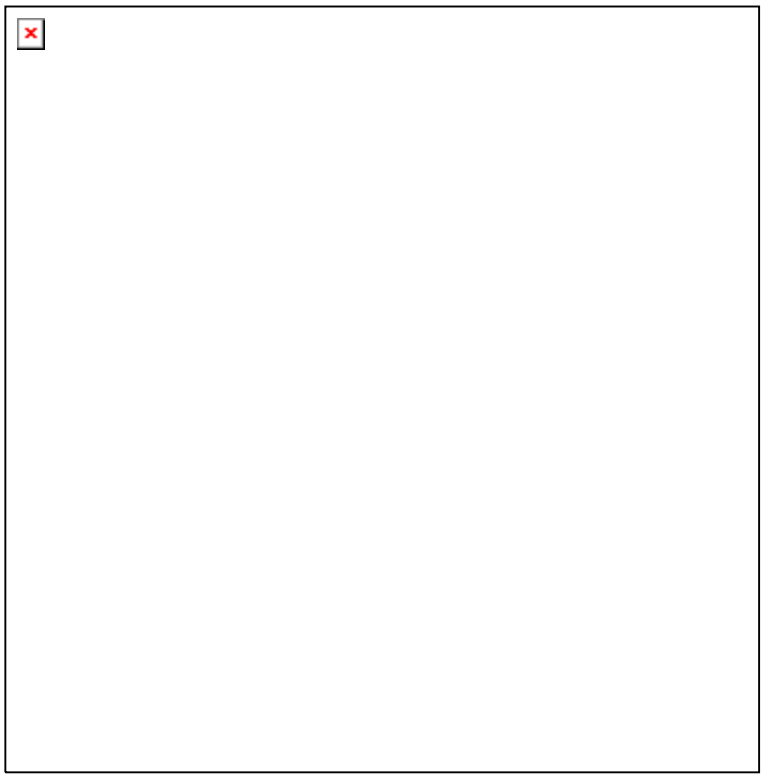

Fig.1. Experimental dependences of thermo-emf coefficient in *PbSe* crystals on partial pressure of the vapors of selenium under the temperature of annealing *T,* K: 1 - 900, 2 – 1000, 3 – 1100.

– the crystals of *PbSe*. After the preliminary warming-up in the vacuum under the temperatures 423-473 K and by the filling of the spectrally clear argon (to $6.6 \cdot 10^3 \div 1.3 \cdot 10^4$ Pa), the ampule was soldered and placed into twozone oven. The partial pressure of the vapor of *Se* was set by the temperature of its warming-up. The temperature of *PbSe* crystals anneal was set by the second zone. It made up 900-1300 K. The time of annealing made up 8-16 hours. After the anneal the ampule with the models was quickly tempered in the ice water. Thermo-emf of such models was measured by the compensation method under 300 K.

The received experimental results are given in figure 1. Obviously that with the increasion of the partial pressure of chalcogen P_{Se_2} under constant temperature of annealing, thermo-emf changes its sign from negative into positive (the inversion of the conducting sign from n- to p-type takes place). The increasing of the temperature of annealing lends to the increasing of the partial pressure of selenium $P_{Se_2(n-p)}$ at which the thermodinamic n-p-transition comes (fig.1). On the basis of the received results (fig.1) the dependence of $P_{Se_2(n-p)}$ on the temperature of anneal (fig.2) is determined. The received dependence approximate by the expression

$$\lg P_{Se_2(n-p)} = 6{,}69 - \frac{8706}{T}. \qquad (1)$$

III. Theoretical framework

Balanced condition of own atomic defects of the *PbSe* crystals at their annealing can be described by a system of crystallochemical equations (table). Here: *V* – vapor; Pb_{Pb}, Se_{Se} – atoms in the assembly; Pb_i, Se_i – interstition atoms; V_{Pb} – vacancies; *e* – electrons; *h* – holes; +,- – charges.

In the proposed model the reaction III – creation of Frenkel pairs in the metal sublattice; reaction II – transition of selenium from vapor into crystal; reactions III-IV – ionization of interstition atoms of lead and vacancies of lead accordingly, reaction V – formation of own conductivity and VI – equation of electroneutrality.

The thermodynamic n-p-transition is

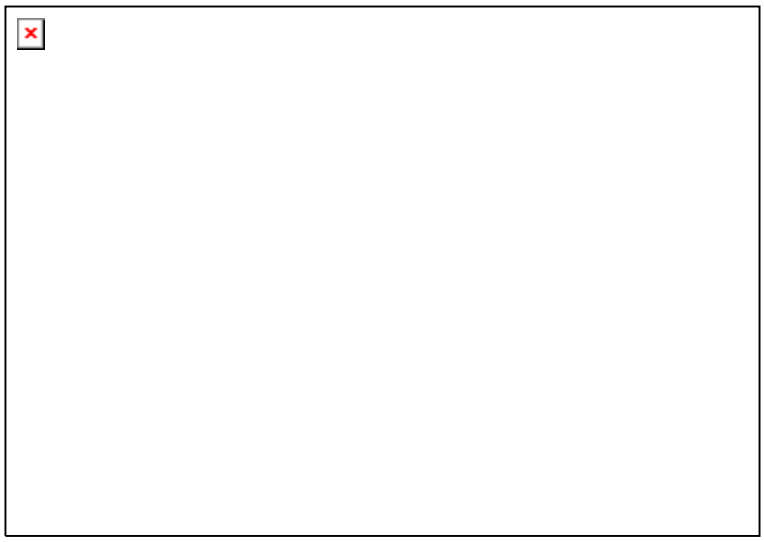

Fig.2. The dependence of partial pressure of the vapor of selenium $P_{Se_2(n-p)}$, for n-p-transition in *PbSe* crystals on the temperature of annealing: **o** - experimental, – - calculation (5).

realized on condition that $n = p$, or according to VII (table):

$$[V_{Pb}^{i}] = [Pb_i^{+}]. \qquad (2)$$

The combined solution of I-V (table) gives opportunity to determine the concentration of vacancies $[V_{Pb}^{-}]$ and interstition atoms $[Pb_i^{+}]$ of lead with the help of the constantts of balance and partial pressure P_{Se_2}

$$[V_{Pb}^{-}] = K_b K_{Se_2,V} \cdot P_{Se_2}^{1/2} K_i^{-1} \cdot n, \qquad (3)$$

$$[Pb_i^{+}] = K_a K_F n^{-1} K_{Se_2,V}^{-1} P_{Se_2}^{-1/2}. \qquad (4)$$

Then with the according of (3) and (4) on the basis of (2) on the condition that $P_{Se_2} = P_{Se_2(n-p)}$, we receive the equation:

$$P_{Se_2(n-p)} = K_a K_F K_b^{-1} K_{Se_2,V}^{-2}. \qquad (5)$$

The Hall concetration of charge carriers n_H, which is determined during the experiment, we'll find on condition that $n_H = n - p$. Accounting V (table), that $p = K_i n^{-1}$, we'll have:

$$n_H = n - K_i n^{-1}. \qquad (6)$$

According to the condition of electroneutrality (VI table), and also (3) and (4), we'll get, that:

$$n^2(T, P_{Se_2}) = (K_i + K_a K_F K_{Se_2,V}^{-1} P_{Se_2}^{-1/2})(1 + K_b K_{Se_2,V} P_{Se_2}^{1/2} \cdot K_i^{-1})^{-1}. \qquad (7)$$

The last equation gives opportunity to determine the concetration of electrons $n_H > 0$ or holes $n_H < 0$ depending on the annealing temperature T and partial pressure of the vapor P_{Se_2}

The results of theoretical calculations according to (5) and (7) are given in figures 2,3,4.

It should be marked, that they fully conside with the received experimental results for n-p-transition (fig.2), and the datas of the works [6-8] (fig.3).

IV. Discussion

The proposed crystallochemical mechanism of formation of own atomic defects in the PbSe crystals gives the opportunity to explain the experimental results of twotemperature anneal. So, the increasing of partial preassure of chacogen vapor brings to the concentration increasing of negatively charged vacancies of lead $[V_{Pb}^{-}]$ and holes (table). It condition the compensation of electrons in the n-type material, the inversion of the conductivity from

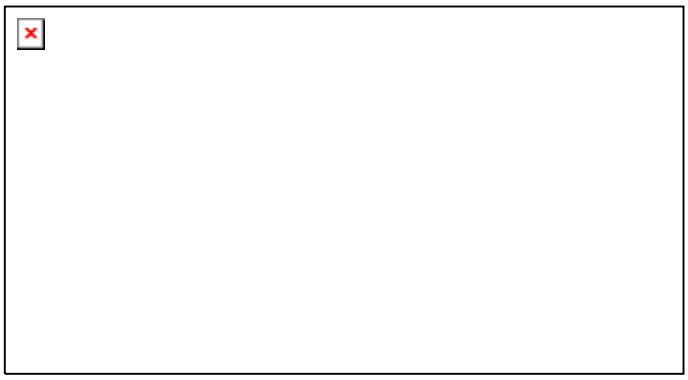

Fig.3. The dependence of the charge carrier concentration in *PbSe* crystals on partial pressure of the vapor of selenium (o - experimental, – - calculation on (7)) under the temperature of annealing *T*, K: 1 – 900, 2 – 990, 3 – 1100.

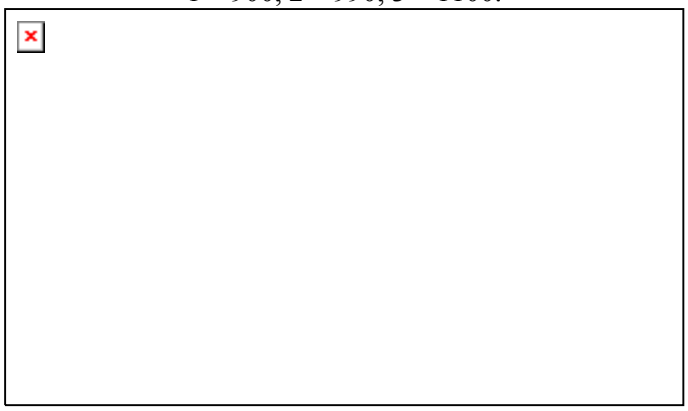

Fig.4. The dependence of the charge carrier concentration in *PbSe* crystals on the temperature of annealing (calculation on (7)) under partial pressure of the vapor of selenium P_{Se_2}, Pa: 1 – 0.1, 2 – 1, 3 – 10.

Table

Crystallochemical equations and the constants of balance $K = K_0 \exp(-\Delta H / kT)$ used during annealing of *PbSe*

№	Equations	Constants	K_0 cm^{-3}, Pa	ΔH, eV
I	$Pb_{Pb} = Pb_i + V_{Pb}$	$K_F(T_1) = [Pb_i][V_{Pb}]$	$6{,}71 \cdot 10^{43}$	2,11
II	$\frac{1}{2} Se_2^V = Se_{Se} + V_{Pb}$	$K_{Se_2,V}(T_1) = [V_{Pb}] P_{Se_2}^{-1/2}(T_2)$	$4{,}05 \cdot 10^{18}$	0,21
III	$Pb_i = Pb_i^+ + e^-$	$K_a(T_1) = [Pb_i^+] n [Pb_i]^{-1}$	$2{,}12 \cdot 10^{20}$	0,14
IV	$V_{Pb} = V_{Pb}^- + h^+$	$K_b(T_1) = [V_{Pb}^-] p [V_{Pb}]^{-1}$	$2{,}12 \cdot 10^{20}$	0,14
V	$0 = e^- + h^+$	$K_i(T_1) = np$	$1{,}13 \cdot 10^{40}$	0,59
VI	$n + [V_{Pb}^-] = p + [Pb_i^+]$			

n- into p-type and the future increasing of the hole concetration (fig.3). The increasing of annealing temperature intensifies the processes of creation of interstition and ionization lead atoms (table). And that's why the thermodynam n-p-transition takes place under higher partial pressures of the chacogen vapor (fig. 2,3).

The change of thermo-emf coefficient by the magnitude and sign (fig. 1) corresponds to the defect condition of the crystals (fig.3) and, accordingly, the concetration of charge carriers. It should be marked, that the received expression (1) and (5) fully conside.

The result of theoretical calculations (5) and (7), and also their graphical presentation (fig.2,3) and experimental datas (fig.1,2) give opportunity to determine the significance of technological factors (the temperature of annealing *T*, partial pressure of chalcogen vapor P_{Se_2}) of twotemperature annealing, which provide the receiving of *PbSe* crystals with the type of conductivity set before hand and the concentration of charge carriers.

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Кристалохімія власних атомних дефектів і термодинамічний *n-p*-перехід у кристалах *PbSe*

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Досліджено *n-p*-перехід у кристалах *PbSe* при двотемпературному відпалі. Експериментальні результати пояснено утворенням власних атомних дефектів міжвузлових атомів свинцю (Pb_i^+), та вакансій свинцю (V_{Pb}^-). Одержано аналітичний вираз, що визначає парціальний тиск пари халькогену, який відповідає термодинамічному *n-p*-переходу, а також залежність концентрації носіїв струму від температури відпалу та парціального тиску пари селену. Визначено технологічні умови формування кристалів *PbSe* із наперед заданими електричними властивостями.

Ключові слова: кристали *PbSe*, дефекти, константа рівноваги, *n-p*-перехід, відпал.