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THERMODYNAMIC ANALYSIS AND DEFECTION FORMATION IN ALLOYS ON THE BASIS OF LEAD SELENIDE CONTAINING COPPER**A.N. Mamedov^{1,2}, N.Ya. Akhmedova², C.M. Asadov¹,
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The process of crystallization of the PbSe liquidus surface in the Cu – Pb – Se system was investigated. Equations were obtained to calculate the partial excess energy functions of mixing lead and selenium for Cu – Pb – Se alloys saturated with lead selenide. The obtained analytical dependences $T - x - y$ and $p(\text{Se}_2) - T - x$ were visualized. It found that when describing the effect of selenium partial pressure on Gibbs partial molar free energy at high pressure, it is necessary to take into account the contribution of the volumetric member. Changes in the energy of defect formation from the electronic chemical potential function in samples based on PbSe in Cu – Pb – Se were studied. Proceeding from the constructed Cu – Pb – Se phase diagram of the isothermal section, a single phase region was determined based on PbSe and two phase regions between PbSe and copper selenides.

Keywords: *thermodynamics, phase equilibrium in Cu – Pb – Se, defect formation energy, doped samples.*

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INTRODUCTION

Materials based on lead and copper chalcogenides are of interest for the production of semiconductor, photovoltaic and thermoelectric elements [1-3]. The following compounds are present in the Pb – Se and Cu – Se systems, respectively: PbSe and Cu₂Se, Cu₃Se₂, CuSe, CuSe₂ [4,5]. Their use in electronics imposes special requirements on properties and quality of structure of the obtained materials. The above stated is confirmed by advances in the synthesis of materials with controlled properties based on PbS [6], PbSe [7] and Cu₂Se [8].

Dopants are a key factor to control properties of semiconductors under various applications. Impurities, for example, make it possible to control the carrier sign and the density of the charge state. In a semiconductor with an ideal doping impurity, an excess charge is directly related to the concentration of the doping impurity. In PbSe, the should be noted that lead chalcogenides with a

replacement metal atom, for example, Na, for the Pb atom is an ideal p-type dopant, since each Na atom brings one additional hole. However, the use of PbSe:Na material is limited which is due to the precipitation of the dopant Na and the formation of the secondary phase of the impurity [9]. This sort of formation and evolution of undesirable secondary phases damage the stability and purity of the PbSe:Na material. The phase diagram of multicomponent systems provides important information about design of the material active in solving the problems above. However, experimental phase diagrams of ternary and complex systems at high pressures or involving non-stoichiometric phases are not always available or available without sufficient details in the area of interest. Such being the case, phase diagrams are calculated to provide alternative recommendations and assist in developing new materials [10]. It rock salt structure are of photoelectric [11] and

thermoelectric materials [12] to be used within the range of 600–900 K [13] where their zT exceeds 1 for p-type materials [14]. Given this, metallic impurities in PbSe can exert control over the concentration of hole carriers [12]. This leads to zT close to 1 at 850 K in PbSe [14]. For Cu–Pb–Se ternary alloys, data on the crystallization surface and thermodynamic characteristics associated with high pressure conditions, as well as characteristics of defect

formation based on binary compounds, are difficult to obtain experimentally and are absent for Cu–Pb–Se alloys [15]. In this study, a thermodynamic approximation of the liquidus surface of phase diagram of the Cu – Pb – Se system at high pressure was performed. The thermodynamics of defects of ideal dopants in a PbSe semiconductor with a narrow band gap (~ 0.3 eV) was analyzed.

EXPERIMENTAL PART

To construct the liquidus surface of the Cu – Pb – Se phase diagram, we studied ternary alloys. The initial compounds Cu_2Se , CuSe and PbSe were synthesized by fusing elementary components of high purity in stoichiometric ratios in the evacuated $\sim 10^{-2}$ Pa and sealed quartz ampoules. To obtain a stoichiometric Cu_2Se composition, after quenching, a hardening was performed at 1300 K in cold water. Following the synthesis, an incongruently melting CuSe compound was annealed at 600 K for 500 h. The individuality

of the synthesized compounds was controlled by means of differential thermal analysis (DTA) (a device for thermal analysis NETZSCH-404 F1 Pegasus system) and X-ray phase analysis (XRD) (D8 ADVANCE diffractometer Bruker, CuK_α -radiation). Alloys of the Cu – Pb – Se system along with Cu_2Se – PbSe, Cu_2Se – Pb, Cu – PbSe, CuSe – PbSe sections were prepared by fusing the initial binary compounds and Cu (Pb) elements in evacuated quartz ampoules using the procedure [16–18].

THEORETICAL PART

The calculation of the energy of defect formation Cu – Pb – Se was carried out on the basis of the density functional theory (DFT) [19, 20] which provides information on the properties of weakly doped semiconductors [21]. The limits of the solubility of the Cu dopant in the PbSe phase in the Cu – Pb – Se system were determined using DFT through the calculation of formation energies of internal and external defects consisting of

$$\Delta E_{d,q} = [E_{d,q} - E_H] + \sum_{\alpha} n_{\alpha}^d (\mu_{\alpha}^0 + \Delta\mu_{\alpha}) + q(E_{V_{BM}} + \Delta V_{PA} + \mu_s) + \Delta E_{IC} \quad (1)$$

where $E_{d,q}$ and E_H – the total energy of the DFT of the PbSe sublattice containing the PbSe sublattice, and the pure PbSe sublattice, respectively, n_{α}^d – amount added ($n_{\alpha}^d = -1$) or removed ($n_{\alpha}^d = +1$) atoms from the pure sublattice for defect formation, μ_{α}^0 is the chemical potential of element α in its standard state, $\Delta\mu_{\alpha}$ is the change in chemical potential α corresponding to a specific phase equilibrium between PbSe and other components in the Cu – Pb – Se system. $E_{V_{BM}}$ is the energy of the maximum of valence band

vacancies (V_{Pb} , V_{Se}), substitution defects (Se_{Pb} , Pb_{Se}) and interstitial defects (Se_i , Pb_i). Defects consisting of Cu substitution defects on Pb or Se (Cu_{Pb} , Cu_{Se}), as well as interstitial defects Cu (Cu_i), all in neutral and charged states from -2 to +2, were taken into account. The equation for calculating the energy of formation of the defect d and the charge q has the form [22]

(VBM) and corresponds to the energy of the highest occupied level. ΔV_{PA} is the potential equalization correction factor (PA) used to re-level the energy rates of defects with the energy levels of the host sublattice and is calculated using $\Delta V_{PA} = \overline{(V_{d,q}^r - V_H^r)}$ [23], where $V_{d,q}^r$ and V_H^r – spherically-averaged electrostatic potentials of supercomplexes of defects and hosts, respectively, far from the place of defect, in order to avoid any side chemical interactions with it. The correction

potential equalization coefficient ranges from +0.08 eV to -0.13 eV for various charged defects. ΔE_{IC} is the energy term of the image correction of the charge that is added to the energy of defect formation in order to simulate the charge of an isolated defect in a sublattice of limited size under non-degenerate conditions and is calculated using [24]. Owing to the relatively high dielectric constant of PbSe, the value of ΔE_{IC} has a maximum value of ~ 7 meV at $q \pm 2$ charges and, thus, has a minimal effect on the value of the formation energy of defects in the calculations. Finally, the value of μ_e in equation (1) is an electronic chemical potential which is the additional energy of electrons in our system. As for graphs showing changes in the energy of defect formation as a function of electronic chemical potential, the value of μ_e was set in the range of the VBM energy values and the minimum of the conduction band. The value of μ_e was calculated as a function of temperature

T and sets of chemical potentials by solving the charge neutrality condition [9]. DFT calculations of energy of defects and sublattices of host atoms were performed using density perturbation theory [25]. Ion-electron interactions were described using self-consistent wave potential method [26]. Electrons Pb: $5d^{10}6s^26p^2$, Se: $4s^24p^4$ and Cu: $3d^{10}4s^1$ taken as valence states in the potentials of self-consistent field. All calculations for the sub-lattices were performed on the selected $5 \times 5 \times 5$ sub-lattice of the primitive cell, which contained 250 atoms. The cutoff energy of the flat wave base was set to 400 eV; for electron smearing, a Gaussian spreading width of 0.1 eV was used [27]. The thermodynamic properties of phases in the $p - T - x$ phase diagram [2, 3] of the Cu - Pb - Se system were described within the model of non-molecular solutions of semiconductors [28, 29] using reference data [30].

RESULTS AND DISCUSSION

$\text{Cu}_2\text{Se} - \text{PbSe}$ is a quasi-binary cross section of the Cu - Pb - Se system. The system is of the eutectic type. The solubility of Cu_2Se in PbSe and PbSe in Cu_2Se is less than 2 mol. %. Eutectic composition is 13.5 mol. % Pb, 38 mol.% Se to get crystallized at 873K (Fig. 1). It was established that the Cu - Pb - Se liquidus surface consists of fields corresponding to the primary crystallization of

Cu, the phase based on the high-temperature modification of Cu_2Se , and PbSe-based phase. Fig. 1 shows areas of Cu (1), Cu_2Se (2), PbSe (3), as well as areas of separation of alloys ($L_1 + L_2$), coordinates of eutectic (e), monotectic (m) and peritectic points (p). Of particular practical interest are coordinates of crystallization of PbSe and Cu_2Se compounds.

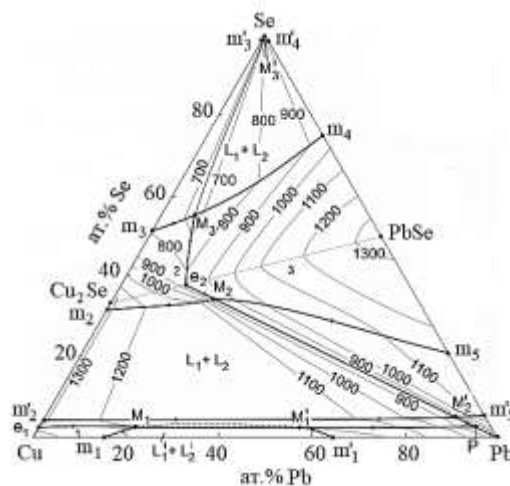


Fig. 1. Projection of the liquidus surface of the Cu - Pb - Se system.

First, we analyze the surface of PbSe crystallization in the Cu - Pb - Se ternary

system. PbSe crystallization surface in the Cu – Pb – Se system within the framework of the

model of non-molecular solutions [28, 29] is approximated by the equation

$$\Delta G_T^{exs,L}(\text{PbSe}) = \Delta H_{298}^0(\text{PbSe}) - \Delta S_{298}^0(\text{PbSe}) - \Delta c_{p,298} T \left[\ln\left(\frac{T}{298}\right) + \left(\frac{298}{T}\right) \right] - RT \ln x_{\text{Pb}} x_{\text{Se}} \quad (2)$$

where $\Delta G_T^{exs,L} = \Delta \bar{G}_{\text{Pb}}^{exs,L} + \Delta \bar{G}_{\text{Se}}^{exs,L}$; $\Delta \bar{G}_{\text{Pb}}^{exs,L}$, $\Delta \bar{G}_{\text{Se}}^{exs,L}$ and x_{Pb} , x_{Se} – partial excess free energies and molar fractions of Pb and Se components in a liquid solution, saturated with PbSe compound; ΔH_{298}^0 , ΔS_{298}^0 – enthalpy and entropy of the formation of PbSe compounds

from liquid components; T is the liquidus temperature, R is the universal gas constant. The calculation of $\Delta G_T^{exs,L}$ in the liquidus line of the PbSe compound in the Pb – Se binary system is determined by the expression:

$$\Delta G_T^{exs,L} = -110693 + 25.695T - RT \ln x_{\text{Pb}} x_{\text{Se}} \quad (3)$$

To change the temperature of PbSe crystallization surface on the composition of

the components in the Cu – Pb – Se ternary system with due regard for (3), we obtain

$$T = \frac{110693 + (1 - x_{\text{Cu}})^{0.35} \Delta G_{\text{PbSe}}^{exs}(x_{\text{Se}}^L)}{25.693 - 8.31 \ln x_{\text{Se}} (1 - x_{\text{Se}})} \quad (4)$$

Where $\Delta G_{\text{PbSe}}^{exs}(x_{\text{Se}}^L)$ – the sum of the partial excess molar free energies of lead and selenium is calculated by equation (3) based on the coordinates of the PbSe liquidus curve. As for the asymmetric dependence (4), the value of the degree 0.35 takes into account changes in the crystallization temperature of PbSe as a function of the copper concentration in the Cu – Pb – Se melts which is determined

on the basis of DTA samples from the Cu – PbSe section.

Using dependences of the partial pressure of saturated selenium vapor [2, 3] and copper concentration on the temperature on the liquidus surface of Cu – Pb – Se for the PbSe – Se (I) and PbSe – Pb (II) regions, we obtain (5) and (6) respectively

$$\lg p_{\text{Se}_2}, (Pa) = \left[\begin{array}{l} -1281 + 5624 \left(\frac{1000}{T}\right) - 9190 \left(\frac{1000}{T}\right)^2 + \\ + 6648 \left(\frac{1000}{T}\right)^3 - 1797 \left(\frac{1000}{T}\right)^4 - 10.35 x_{\text{Cu}}^2 \end{array} \right] \quad (5)$$

$$\lg p_{\text{Se}_2}, (Pa) = \left[\begin{array}{l} 2026 - 8778 \left(\frac{1000}{T}\right) + 14247 \left(\frac{1000}{T}\right)^2 - \\ - 10259 \left(\frac{1000}{T}\right)^3 + 2759 \left(\frac{1000}{T}\right)^4 - 8.36 x_{\text{Cu}}^2 \end{array} \right] \quad (6)$$

The constructed PbSe crystallization surface in Cu – Pb – Se at high pressure,

taking into account equations (5) and (6), is shown in Fig. 2.

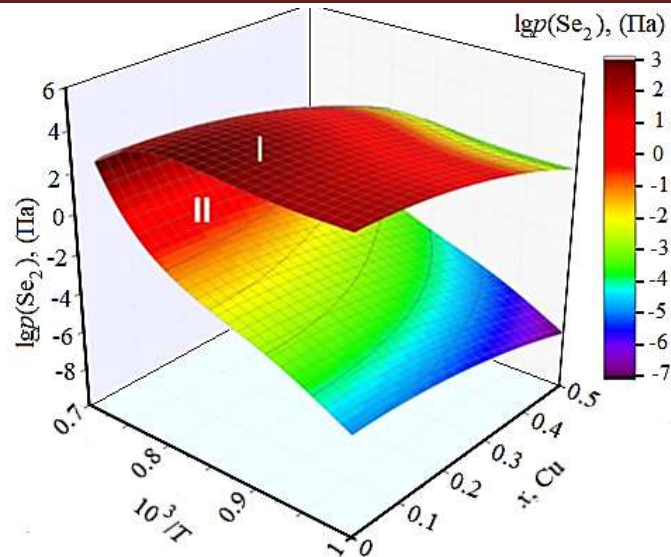


Fig. 2. Projections of the $p - T - x$ phase diagram for the partial pressure of the saturated vapor Se_2 over the PbSe liquidus surface in the $\text{Cu} - \text{Pb} - \text{Se}$ ternary system. I is the $\text{PbSe} - \text{Se}$ region (by equation 5), II is the $\text{PbSe} - \text{Pb}$ region (by equation 6).

From the $T - x$ phase diagram of $\text{Pb} - \text{Se}$ [2, 3], it follows that the melting point of PbSe (1352 K) corresponds to the non-stoichiometric composition of PbSe_{1-x} while

lead selenide has a narrow homogeneity range. In considering that the liquid phase L and the PbSe -based solid solution phase S are in equilibrium, we obtain

$$\mu_{iL}(T, p, x_{iL}) = \mu_{iS}(T, p, x_{iS}) \quad (7)$$

where μ_{iL} , μ_{iS} —chemical potentials of component i in phases L and S , respectively. As a standard state, we choose the pure solid or liquid state of component i . Then the

chemical potential (Gibbs partial molar free energy) of component i in the liquid phase $\mu_{iL}(T, p, x_{iL})$ or solid solution $\mu_{iS}(T, p, x_{iS})$ is determined by the ratio

$$\mu_{iL}(T, p, x_{iL}) = \mu_{iL}^0(T, p_0) + RT \ln x_{iL} \gamma_{iL}(T, p_0, x_{iL}) + \int_{p_0}^p \bar{V}_{iL}(T, p, x_{iL}) dp \quad (8)$$

where ($i = 1, 2$).

From equation (8), it follows that in terms of high partial pressure of vapors of the components, it is also necessary to take into account the influence of the volume term \bar{V}_{iL} on the Gibbs partial molar free energy of component i .

If we consider that PbSe -based surface crystallization in $\text{Cu} - \text{Pb} - \text{Se}$ is characterized by asymmetric appearance, the excess molar volume is determined by the Hillert method, as follows

$$V_m^E = \frac{x_2}{1-x_1} V_{12}^E(x_1, 1-x_1) + \frac{x_3}{1-x_1} V_{13}^E(x_1, 1-x_1) + \frac{x_2 x_3}{\omega_{23} \omega_{32}} V_{23}^E(\omega_{23}, \omega_{32}) \quad (9)$$

$$\omega_{23} = \frac{1+x_2-x_3}{2}; \quad \omega_{32} = \frac{1+x_3-x_2}{2}; \quad \omega_{23} + \omega_{32} = 1 \quad (10)$$

where V_{12}^E , V_{13}^E and V_{23}^E are excess molar volumes for three components of the system, Since

V_m^E is excess molar volume for the ternary system.

$$\bar{V}_i^E = V_m^E + \frac{\partial V_m^E}{\partial x_i} - \sum_{j=1}^3 x_j \frac{\partial V_m^E}{\partial x_j}, (i = 1,2,3)$$

$$\bar{V}_i = V_i^0 + \bar{V}_i^E (i = 1,2,3), \quad (11)$$

then the partial molar volume $\bar{V}_i(T, p_0, x_i)$ for component ion on the surface of crystallization in the Cu – Pb – Se system is determined by the values of V_{ij}^E for three components ($i= 1$ (PbSe), 2(Cu₂Se), 3(Cu)).

Finally, at high pressure, when adjusted for the activity coefficient γ_i of a component, the equation of phase equilibrium at the liquid / PbSe (S₂)- based solid solution interface is determined by the following expression

$$\frac{x_{iL} \gamma_{i,L}(T, p_0, x_{i,L})}{x_{iS_2} \gamma_{i,S_2}(T, p_0, x_{i,S_2})} = \exp\left(-\frac{\mu_{i,L}^0 - \mu_{i,S_2}^0}{RT}\right) \times \exp\left\{\frac{1}{RT} \int_{p_0}^p [\bar{V}_{i,S_2}(T, p, x_{i,S_2}) - \bar{V}_{i,L}(T, p, x_{i,L})] dp\right\} \quad (12)$$

Below, we consider the results of calculating the energy of defect formation in Cu – Pb – Se. It has been established that the energy of formation of Cu_{Pb}^0 defects is negative (-0.152 eV) in three of four areas of three-phase equilibria: PbSe – Cu₂Se – CuSe, PbSe – CuSe – CuSe₂ and Se – PbSe – CuSe₂. The calculated negative energies of formation of neutral defects, which are independent on μ_e , indicate a zero doping efficiency and do not represent the supposed defect.

the energy of defect formation with the lowest energies of intrinsic and unrealistic defects in PbSe as functions of the Fermi level in the Pb – PbSe – Cu equilibrium regions of the Cu – Pb – Se phase diagram. Solid lines indicate defects included in the calculation of the Cu – Pb – Se phase diagram, while dashed lines indicate unrealistic defects. Considering this, when calculating phase diagrams and doping efficiency in line with the experiment, it is necessary to use only the expected charge states for each defect.

Fig. 3 shows the typical dependence of

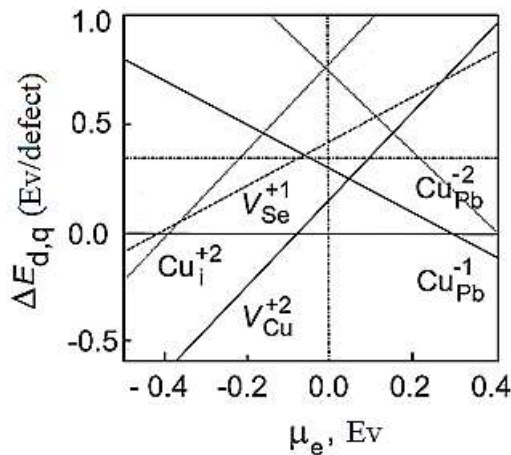


Fig.3. Energy of formation of intrinsic defects $\Delta E_{d,q}$ and unrealistic defects in PbSe depending on the Fermi level, μ_e (relative to the energy of the maximum of the valence band-VBM) in the three-phase equilibrium region Pb – PbSe – Cu phase diagram Cu – Pb – Se. Solid lines indicate defects included in the calculation of the Cu – Pb – Se phase diagram, while dashed lines indicate unrealistic defects.

Thus, standard calculations of the energy of defect formation in PbSe with an

admixture of Cu p-type show that defects with unexpected charge states lead to low energy of defect formation, which do not agree with the experimentally observed PbSe doping efficiency [11]. This can be traced to the charge delocalization, which changes the charge state of the calculated defect.

Excluding unrealistic defects, in particular, marked with dotted lines in Fig. 3, an isothermal section was constructed characterizing the boundaries of the PbSe-based solid phase at 573 K on the Cu–Pb–Se diagram (Fig. 4).

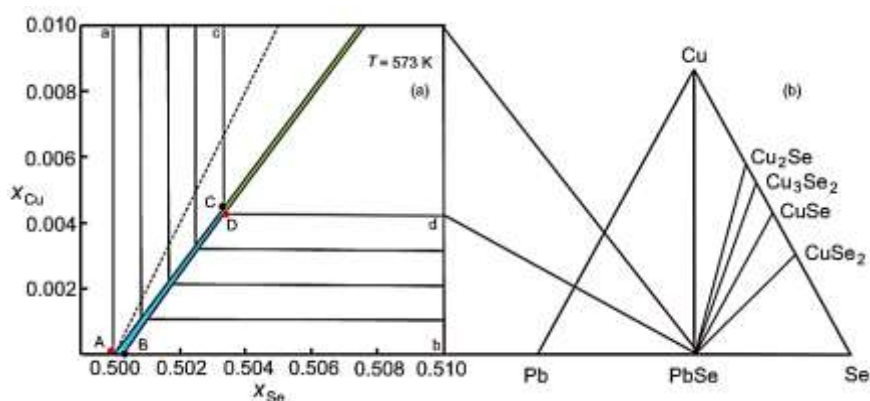


Fig. 4. An isothermal section of the Cu – Pb – Se phase diagram, built at 573 K, shows PbSe-based single-phase region, as well as connection lines representing two-phase regions between PbSe and other binary Cu – Se compounds which are shown in the full isothermal section (b).

In Fig. 4a, the dotted line represents the path between PbSe and Cu for a one-to-one substitution of Pb with Cu, that is $\text{Pb}_{1-x}\text{Cu}_x\text{Se}$. Point B denotes the coordinate of the maximum solubility of Cu in the three-phase Pb – PbSe – Cu region where it is admitted that the sample demonstrates n-type conductivity. Point D indicates the solubility coordinate of Cu in the three-phase Pb – PbSe – Cu region where it is obvious that the sample exhibits p-type conductivity.

The isothermal section of the Cu – Pb – Se phase diagram, calculated at $T = 573$ K, also shows PbSe-based single-phase region in A – B – C – D region (Fig. 4a). Straight lines in the A – a – c – B and B – D – d – b regions are two-phase regions between PbSe and other Cu – Se compounds which are shown in the full isothermal region (b). Thus, equations for calculating the partial excess energy functions of the mixing of lead and selenium for Cu – Pb – Se alloys saturated with lead selenide were obtained. Taking into account the constructed

surface of crystallization of the components in the Cu – Pb – Se system and the obtained $T - x - y$ and $p(\text{Se}_2) - T - x$ dependences, the visualization and thermodynamic analysis of these dependences were performed. In describing the effect of pressure on the Gibbs partial molar free energy and phase equilibrium at high pressures of the Cu – Pb – Se system, it is necessary to take into account the asymmetric appearance of the volume term. The dependence of the formation energy of intrinsic and unrealistic defects in PbSe-based samples as a function of the Fermi level in Cu – Pb – Se was constructed. The constructed isothermal section of the Cu – Pb – Se phase diagram enables to determine, PbSe-based single-phase region and two-phase regions between PbSe and other Cu – Se compounds. In particular, in case of one-to-one substitution of Pb for Cu, the points of maximum solubility of Cu in the three-phase Pb – PbSe – Cu region where the types of conductivity of the samples were determined.

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ТЕРМОДИНАМИЧЕСКИЙ АНАЛИЗ И ДЕФЕКТООБРАЗОВАНИЕ В СПЛАВАХ НА ОСНОВЕ СЕЛЕНИДА СВИНЦА, СОДЕРЖАЩИХ МЕДЬ

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Исследован процесс кристаллизации поверхности ликвидуса PbSe в системе Cu–Pb–Se. Получены уравнения для расчета парциальных избыточных функций энергии смешения свинца и селена для сплавов Cu–Pb–Se, насыщенных селенидом свинца. Проведена визуализация полученных аналитических зависимостей $T-x-y$ и $p(\text{Se}_2)-T-x$. Показано, что в описании влияния парциального давления селена на парциальную молярную свободную энергию Гиббса при высоком давлении необходимо учесть вклад объемного члена. Изучено изменение энергии образования дефектов от функции электронного химического потенциала в образцах на основе PbSe в Cu–Pb–Se. На основе построенного изотермического разреза фазовой диаграммы Cu–Pb–Se определены однофазная область на основе PbSe и двухфазные области между PbSe и селенидами меди.

Ключевые слова: термодинамика, фазовые равновесия в Cu–Pb–Se, энергия образования дефектов, легированные образцы.

TƏRKİBİNDƏ MİS OLAN QURĞUŞUN SELENİD ƏSASLI XƏLİTƏLƏRİN TERMODİNAMİKİ ANALİZİ VƏ ONLARDA DEFEKT ƏMƏLƏGƏLMƏ

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Cu-Pb-Se sistemində PbSe-in likvidus səthi üzrə kristallaşma prosesi tədqiq edilmişdir. Cu-Pb-Se sisteminin qurğuşun sulfidlə doymuş xəlitələrində qurğuşun və selenin parsial izafi sərbəst enerjisini hesablamaq üçün tənliklər çıxarılmış, $T-x-y$ və $p(\text{Se}_2)-T-x$ asılılıqlarının analitik ifadələrinin 3D görüntüləri alınmışdır. Müəyyən edilmişdir ki, selenin parsial təzyiqinin Gibbs sərbəst enerjisinə təsirini müəyyən etmək üçün bərk fazanın həcm dəyişməsinin payını nəzərə almaq lazımdır. Cu-Pb-Se sistemində PbSe əsaslı xəlitə nümunələrində defektlərin əmələgəlmə enerjisinin elektron potensialından asılılıq funksiyası öyrənilmişdir. Cu-Pb-Se sisteminin faza diaqramının izotermik kəsiyində PbSe-in homogenlik sahəsi və onun mis sulfidləri ilə əmələ gətirdiyi iki fazalı sahələr təyin edilmişdir.

Açar sözlər: termodinamika, faza tarzlığı, Cu–Pb–Se sistemi, parsial təzyiq, defekt əmələ gəlməsi