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The equilibrium phase space of the Ag–In–Se system in the part AgInSe–InSe–Se below 500 K consists seven three-phase regions In$_2$Se–AgIn$_2$Se$_7$–Se (I), AgIn$_2$Se$_7$–AgInSe$_5$–Se (II), AgInSe$_5$–AgInSe$_5$–Se (III), In$_2$Se–In$_2$Se–In$_2$Se–AgIn$_2$Se$_7$–AgInSe$_5$–Se (IV), In$_2$Se–AgIn$_2$Se$_7$–AgInSe$_5$–Se (V), In$_2$Se–In$_2$Se–AgIn$_2$Se$_7$–AgInSe$_5$–Se and In$_2$Se–AgIn$_2$Se$_7$–AgInSe$_5$–Se (VI). Division of the AgInSe–InSe–Se into separate phase regions was performed based on electromotive force vs temperature dependences of six electrochemical cells (ECCs) of the type: $\Delta G_{f}^{\circ}(I)$, $\Delta G_{f}^{\circ}(II)$, $\Delta G_{f}^{\circ}(III)$, $\Delta G_{f}^{\circ}(IV)$, $\Delta G_{f}^{\circ}(V)$ and $\Delta G_{f}^{\circ}(VI)$ of forming of the thermodynamically stable set of phases from phase non-equilibrium mixture of compounds specified in (I)–(VI) is carried out in the R(Ag$^+$) region. The Ag$^+$ ions act as the small nucleation centers for stable phases. Based on the temperature dependences of the electromotive force of ECCs with PE of the (I)–(VI) phase regions, the standard thermodynamic functions of the binary In$_2$Se–Se and three ternary compounds in the adjacent phase regions were calculated for the first time. The agreement of the calculated values of the standard Gibbs energies of the AgIn$_2$Se$_5$ compound in two different phase regions (II) and (V): $\Delta G_{f}^{\circ}(II)$ = (819.6 ± 8.9) kJ·mol$^{-1}$ and $\Delta G_{f}^{\circ}(V)$ = (820.0 ± 8.9) kJ·mol$^{-1}$ characterizes the phase composition of the regions (I), (II), (IV), and (V) below 500 K as a combination of compounds of formulaic composition.

Keywords: Ag-containing compounds, Thermodynamic properties, Phase equilibria, Gibbs energy, EMF method.

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Introduction

The T–x diagram Ag$_2$Se–In$_2$Se$_3$ of the Ag–In–Se system features the formation of AgInSe$_2$, AgInSe$_5$, and AgIn$_2$Se$_7$ compounds with congruent 1060 K, 1088 K, and incongruent 1077 K type of melting, respectively [1]. The AgInSe$_2$ and AgInSe$_5$ compounds crystallize from the melt as phases of variable composition, undergo polymorphic transformations at 968 K and 1013 K, respectively. The homogeneity ranges of these compounds are equal to ~3 and ~4 mol.% In$_2$Se$_3$ at the room temperature. The isothermal cross-section of the Ag–In–Se system at 723 K is characterized by the Ag$_2$In, Ag$_2$Se, In$_2$Se$_3$, InSe, In$_2$Se$_7$, In$_2$Se$_5$, AgIn$_2$Se$_7$, and AgIn$_2$Se$_5$ compounds [2]. The existence of AgIn$_2$Se$_7$ compound has not been established. The ternary AgInSe$_2$ and AgInSe$_5$ compounds are evaluated as promising for use in nonlinear optics, manufacturing of visible and infrared LEDs, infrared detectors, solar cells, and other optoelectronic devices [3,4]. Information on the main thermodynamic properties of the ternary phases AgInSe$_2$ and AgInSe$_5$, which are important for the analysis of uncontrolled changes in the operation of scientific and technological equipment, is currently lacking. Presented
in [5,6] data on the standard Gibbs energy of the formation of AgInSe$_2$ and AgIn$_3$Se$_5$ compounds $\Delta_G^o = -188$ kJ mol$^{-1}$ and $\Delta_G^o = -850$ kJ mol$^{-1}$ are approximate because they do not take into account the Gibbs energy of the synthesis reactions $\Delta_G^o$ from the calculated amounts of Ag$_2$Se and In$_2$Se$_3$.

The purpose of this work was to establish the values of standard thermodynamic functions (Gibbs energy, enthalpy, and entropy) of the AgInSe$_2$, AgIn$_3$Se$_5$, AgIn$_2$I$_7$, and In$_2$Se$_7$ compounds by using the EMF method [7–9] and literature data on the thermodynamic properties of the InSe and In$_2$Se$_3$ compounds [10]. The results of calculations of thermodynamic functions of compounds can be used to analyze the reasons for changes in the performance of equipment manufactured with their participation and modeling the phase diagrams of multicomponent systems, including Ag–In–Se, by the CALPHAD methods [11,12].

I. Experimental

The high purity elements Ag, In, and Se (>99.99 wt.%, Alfa Aesar, Germany) were used for synthesis of the compounds. The evacuated melts of the calculated amounts of the elements were well-mixed for 20 min and followed by cooling to the room temperature at a rate of ~5 K min$^{-1}$. Crushed to a particle size of ~5 µm polycrystalline samples were used for X-ray analysis and preparation of positive electrodes of electrochemical cells (ECCs). An STOE STADI P diffractometer equipped with a linear position-sensitive detector PSD, in a Guinier geometry (transmission mode, CuK$\alpha_1$, radiation, a bent Ge(111) monochromator, and 2θ/ω scan mode) was used to establish the phase composition of the samples. The following programs STOE WinXPOW [13], PowderCell [14], FullProf [15], as well as databases [16,17] were used for X-ray phase analysis.

Synthesis of a thermodynamically equilibrium set of compounds below 500 K from a phase non-equilibrium mixture of compounds obtained by cooling the melts and the EMF ($E$) measurements were performed in ECCs type (A):

$$(-)\text{C} | \text{Ag(SE)} | \text{R(Ag$^+$)} | \text{PE} | \text{C(+)}.$$  \hspace{1cm} (A)

where C is the graphite (inert electrode), Ag is the left (negative) electrode, SE is the solid-state electrolyte (Ag$_2$GeS$_4$Br glass), PE is the right (positive) electrode, R(Ag$^+$) is the buffer region of PE that contacts with SE. The process of forming of the thermodynamically stable set of phases from phase non-equilibrium mixture of finely dispersed compounds is carried out in the R(Ag$^+$) region. The Ag$^+$ ions act as the small nucleation centers for stable phases [18].

Components of the ECCs in powder form were pressed at 10$^8$ Pa through a 2 mm diameter hole arranged in fluoroplast matrix up to density $\rho = (0.93 \pm 0.02) \rho_0$, where $\rho_0$ is the experimentally determined density of cast samples [19,20]. The experiments were performed in a horizontal resistance furnace, similar to that described in [21]. As the protection atmosphere we used a flow of highly purified (99.99 volume fraction) Ar (g) at $P = 1.2 \times 10^5$ Pa. The gas flow of Ar at the rate of $10^{-3}$ m$^3$ min$^{-1}$ from the right to the left electrodes of the ECCs. The temperature was maintained with an accuracy of ±0.5 K. The EMF values of the cells were measured using high-resistance (input impedance of >10$^{12}$ Ω) the Picotest M3500A universal digital multimeter. The equilibrium in ECCs at each temperature was achieved within 2 h. During equilibrium the EMF values were constant or their variations were not exceed ±0.2 mV [22]. The dependences of the EMF of the cells on temperature $E(T)$ were analyzed by the method described in [23–25]. The ratios of initials components of PE of ECCs were determined from the equations of potential-forming reactions in respective phase regions.

II. Results and discussion

The alleged scheme division of the concentration space of the Ag–In–Se system in the AgInSe$_2$–InSe–Se region below 500 K, confirmed our investigations of the boundaries of the phase fields by the EMF method, is shown in Fig. 1.

![Fig. 1. Division of the concentration space of the Ag–In–Se system in the AgInSe$_2$–InSe–Se region below 500 K: 1 are lines of two-phase equilibria, 2 are compositions of the positive electrodes of the ECCs in the phase regions (I)–(VI).](image)

The position of the three-phase regions: In$_2$Se$_3$–AgIn$_2$I$_7$–Se (I), AgIn$_2$I$_7$–AgIn$_3$Se$_5$–Se (II), AgIn$_3$Se$_5$–AgInSe$_2$–Se (III), In$_2$Se$_3$–AgIn$_1$I$_7$Se$_7$–In$_2$Se$_7$ (IV), In$_6$Se$_7$–AgIn$_1$I$_7$Se$_7$–AgIn$_3$Se$_5$ (V), In$_2$Se$_7$–AgIn$_3$Se$_5$–AgInSe$_2$ (VI) relative to silver was used to write equations of the overall potential-forming reactions:

$$2\text{Ag} + 11\text{In}_2\text{Se}_3 + \text{Se} = 2\text{AgIn}_1\text{I}_7\text{Se}_7,$$  \hspace{1cm} (R1)

$$6\text{Ag} + 5\text{AgIn}_1\text{I}_7\text{Se}_7 + 3\text{Se} = 11\text{AgIn}_3\text{Se}_5,$$  \hspace{1cm} (R2)

$$4\text{Ag} + 5\text{AgIn}_3\text{Se}_5 + 2\text{Se} = 5\text{AgInSe}_2.$$  \hspace{1cm} (R3)
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\begin{align*}
4\text{Ag} + 25\text{In}_2\text{Se}_3 &= \text{In}_6\text{Se}_7 + 4\text{AgIn}_{11}\text{Se}_{17}, \quad (R4) \\
12\text{Ag} + 13\text{AgIn}_{11}\text{Se}_{17} &= 3\text{In}_6\text{Se}_7 + 25\text{AgIn}_5\text{Se}_8, \quad (R5) \\
2\text{Ag} + \text{AgIn}_5\text{Se}_8 &= 2\text{InSe} + 3\text{AgInSe}_2. \quad (R6)
\end{align*}

Equations (R1)–(R6) were used to establish the ratios of selenium, binary and ternary compounds in PE of ECCs.

The cooled melts of the binary and ternary compounds mentioned in reactions (R1)–(R6) are thermodynamically non-equilibrium. In particular, according to results of X-ray analysis, the cooled melt of the formula composition \(2\text{In}_2\text{Se}_3\) is characterized by two modifications of \(\text{In}_2\text{Se}_3\) with closely related structures (space groups (SG) \(P6_3\) for the \(\text{In}_2\text{Se}_3\) phase, stable under normal conditions, and SG \(P6_1\) for the high-temperature modification of \(\text{In}_2\text{Se}_3\)), and the InSe sample, apart from the InSe compound (SG \(R3m\)), contains impurities of the \(\text{In}_6\text{Se}_7\) phase (SG \(P2_1/m\)), Fig. 2, a, b. The crystallized \(\text{AgIn}_{11}\text{Se}_{17}\) melt contains a set of lines of the \(\text{AgIn}_{11}\text{Se}_{17}\) compound with an uncertain structure and the \(\text{AgIn}_5\text{Se}_8\) (SG \(P-42m\)), Fig. 2, c. The crystallized \(\text{AgIn}_5\text{Se}_8\) contains impurities of the \(\text{AgInSe}_2\), Fig. 2, d. Alloys of the formulas \(\text{In}_6\text{Se}_7\) and \(\text{AgIn}_5\text{Se}_8\) crystallize as single-phase samples.

Newly assembled PE of the ECCs according to

![Fig. 2. X-ray powder diffraction patterns of samples with composition: In\(_2\)Se\(_3\) (a), InSe (b), AgIn\(_{11}\)Se\(_{17}\) (c), and AgInSe\(_2\) (d) (black color). Compositions of the samples and identified phases (with space group indicated) are shown in the upper right corner.](image-url)
equations (R1)–(R6) are the combination of thermodynamically nonequilibrium phases, which cause the formation of the R(Ag\textsuperscript{+}) region in the ECC. The process of forming of the thermodynamically stable set of phases from phase non-equilibrium mixture of finely dispersed compounds for the participation of Ag\textsuperscript{+} ions as a catalyst end in 48 hours at 500 K. The criterion for attaining phase equilibria in the R(Ag\textsuperscript{+}) region of PE is the reproducibility of the E(T) relations of ECCs during the heating-cooling cycles.

The measured EMF values as a function temperature of ECCs are presented in Table 1.

### Table 1

| Phase regions | (I) | (II) | (III) | (IV) | (V) | (VI) |
|---------------|-----|------|-------|------|-----|------|
| 7/K           | E/mV| E/mV | E/mV  | E/mV | E/mV| E/mV |
| 430.3         | 375.1| 367.3| 362.3| 385.7| 374.7| 364.8|
| 435.2         | 375.6| 368.4| 362.9| 386.4| 375.2| 365.2|
| 440.2         | 376.0| 368.9| 363.3| 387.0| 375.8| 365.7|
| 445.2         | 376.3| 369.6| 363.9| 387.7| 376.3| 366.1|
| 450.1         | 376.7| 370.2| 364.4| 388.5| 376.9| 366.6|
| 455.1         | 377.1| 370.9| 365.2| 389.2| 377.5| 367.0|
| 460.0         | 377.5| 371.5| 365.7| 389.9| 378.0| 367.4|
| 465.0         | 377.9| 372.1| 366.1| 390.5| 378.5| 367.9|
| 469.9         | 378.2| 372.7| 366.7| 391.2| 379.1| 368.3|
| 474.7         | 378.6| 373.4| 367.4| 391.9| 379.7| 368.8|
| 479.3         | 379.0| 374.1| 367.8| 392.6| 380.3| 369.3|
| 484.0         | 379.4| 374.7| 368.4| 393.3| 380.9| 369.8|
| 489.6         | 379.9| 375.5| 368.9| 393.9| 381.4| 370.2|
| 494.5         | 380.3+| 376.1| 369.7| 394.7| 381.9| 370.6|

* Data point not included in treatment

The linear dependencies E(T) between 430 K and 494 K provided that Δ\textsubscript{r}G\textsuperscript{p} \textsuperscript{const} and equal zero [23] were calculated by the least squares method and expressed as:

\[
E_{R1}/mV= \left((341.2\pm0.3)+(78.8\pm0.7)\cdot10^{-3}\right)/K, \tag{1}
\]

\[
E_{R2}/mV= \left((311.3\pm0.5)+(130.9\pm1.0)\cdot10^{-3}\right)/K, \tag{2}
\]

\[
E_{R3}/mV= \left((313.2\pm0.6)+(114.1\pm1.3)\cdot10^{-3}\right)/K, \tag{3}
\]

\[
E_{R4}/mV= \left((325.3\pm0.4)+(140.3\pm0.8)\cdot10^{-3}\right)/K, \tag{4}
\]

\[
E_{R5}/mV= \left((325.6\pm0.4)+(113.9\pm0.9)\cdot10^{-3}\right)/K, \tag{5}
\]

\[
E_{R6}/mV= \left((325.3\pm0.4)+(91.6\pm0.8)\cdot10^{-3}\right)/K. \tag{6}
\]

The temperature dependences the EMF of ECCs is presented in Fig. 3.

The correctness of presented in Fig. 1 division of the Ag–In–Se system in the AgInSe\textsubscript{2}–InSe–Se part below 500 K is confirmed by the following provisions:

- E vs T dependences of ECCs with PE of the (I)–(VI) phase regions are characterized by different EMF values at T=const and the intercept and slope coefficients;
- the phase regions that are more distant from the point of Ag are characterized by higher EMF values at T = const.

The Gibbs energies, enthalpies, and entropies of reactions (R1)–(R6) can be calculated by applying the thermodynamic Eqs. (7)–(9):

\[
\Delta\text{r}G = -z \cdot F \cdot E, \tag{7}
\]

\[
\Delta\text{r}H = -z \cdot F \cdot [E - (dE/dT) \cdot T], \tag{8}
\]

\[
\Delta\text{r}S = z \cdot F \cdot (dE/dT), \tag{9}
\]

where z is the number of electrons involved in the reactions (R1)–(R6), F = 96485.33289 C\textsuperscript{-mol\textsuperscript{-1}} is Faraday’s constant, and E is the EMF of ECCs.

The values of thermodynamic functions of the reactions (R1)–(R6) at 298 K and p=10\textsuperscript{5} Pa were calculated using Eqs. (7)–(9). The determined results are listed in Table 2.

The Gibbs energy, enthalpy, and entropy of reaction (R1) are related to the Gibbs energy, enthalpy, and entropy of the AgInSe\textsubscript{2} compound and pure elements of Ag and Se by Eqs. (10)–(12):

### Table 2

| Reaction | \(\Delta\text{r}G^\circ\) | \(\Delta\text{r}H^\circ\) | \(\Delta\text{r}S^\circ\) |
|----------|--------------------------|--------------------------|--------------------------|
|          | kJ\textsuperscript{\text{-mol\textsuperscript{-1}}} | J\textsuperscript{\text{-mol\textsuperscript{-1}}K\textsuperscript{-1}} |
| (R1)     | 70.37 ± 0.74             | 65.84 ± 1.99             | 15.20 ± 2.18             |
| (R2)     | 202.80 ± 1.92            | 180.22 ± 2.25            | 75.78 ± 2.53             |
| (R3)     | 134.00 ± 1.06            | 120.88 ± 2.16            | 44.04 ± 1.33             |
| (R4)     | 141.69 ± 1.18            | 125.55 ± 2.20            | 54.15 ± 1.24             |
| (R5)     | 416.31 ± 3.54            | 376.99 ± 4.58            | 131.88 ± 2.71            |
| (R6)     | 68.04 ± 0.59             | 62.77 ± 1.09             | 17.68 ± 0.61             |
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\[ \Delta_r(R_1)G^\circ = 2\Delta_rG_{AgIn_{11}Se_{17}}^\circ - 11\Delta_rG_{In_{2}Se_3}^\circ, \]  
(10)

\[ \Delta_r(R_1)H^\circ = 2\Delta_rH_{AgIn_{11}Se_{17}}^\circ - 11\Delta_rH_{In_{2}Se_3}^\circ, \]  
(11)

\[ \Delta_r(R_1)S^\circ = 2S_{AgIn_{11}Se_{17}}^\circ - 2S_{Ag}^\circ - 11S_{In_{2}Se_3}^\circ - S_{Se}^\circ. \]  
(12)

It follows from Eqs. (10)–(12) that:

\[ \Delta_rG_{AgIn_{11}Se_{17}}^\circ = 0.5(11\Delta_rG_{In_{2}Se_3}^\circ + \Delta_r(R_1)G^\circ), \]  
(13)

\[ \Delta_rH_{AgIn_{11}Se_{17}}^\circ = 0.5(11\Delta_rH_{In_{2}Se_3}^\circ + \Delta_r(R_1)H^\circ), \]  
(14)

\[ S_{AgIn_{11}Se_{17}}^\circ = 0.5\left(2S_{Ag}^\circ + 11S_{In_{2}Se_3}^\circ + S_{Se}^\circ + \Delta_r(R_1)S^\circ\right). \]  
(15)

Similarly, the corresponding equations to determine \( \Delta_rG^\circ, \Delta_rH^\circ, \) and \( S^\circ \) of the AgInSe\(_8\), AgInSe\(_3\), In\(_2\)Se\(_3\), AgIn\(_2\)Se\(_3\), and AgInSe\(_2\) compounds in the phase regions (II)–(VI) can be written based on reactions (R2)–(R6), with their appropriate stochiometric numbers.

Combining Eqs. (13)–(15), using thermodynamic data of the pure elements Ag, In, Se and binary compounds InSe, In\(_2\)Se\(_3\) [10], the standard thermodynamic data of selected compounds in the Ag–In–Se system were calculated for the first time. A comparative summary of the calculated values together with the available literature data is listed in Table 3.

The coincidence of the calculated values of the thermodynamic functions of the compound AgInSe\(_3\) in the phase sections (II), (V) characterizes the phase composition (I), (II), (IV), (V) below 500 K as a combination of compounds of formulaic composition. The difference in the values of the thermodynamic properties of AgInSe\(_2\) equilibrium in the phase regions (III), (VI) characterizes the ternary compound as a phase of variable composition.

Considering data presented in Table 3, the temperature dependences of the Gibbs energy of formation of the AgIn\(_{11}\)Se\(_{17}\), AgInSe\(_3\), AgInSe\(_2\), In\(_2\)Se\(_3\), and AgInSe\(_3\) compounds in the phase regions (I)–(VI) are described by Eqs. (16)–(21), respectively:

\[ \Delta_rG_{AgIn_{11}Se_{17}}(T)/(kJ\cdot mol^{-1}) = -(1827.8 \pm 20.3) + (218.8 \pm 3.1) \cdot 10^{-3}T/K, \]  
(16)

\[ \Delta_rG_{AgInSe_3}(T)/(kJ\cdot mol^{-1}) = -(847.2 \pm 10.7) + (92.6 \pm 1.6) \cdot 10^{-3}T/K, \]  
(17)

\[ \Delta_rG_{InSe_3}(T)/(kJ\cdot mol^{-1}) = -(193.6 \pm 3.2) + (9.7 \pm 0.2) \cdot 10^{-3}T/K, \]  
(18)

\[ \Delta_rG_{In_2Se_3}(T)/(kJ\cdot mol^{-1}) = -(973.0 \pm 11.3) + (100.0 \pm 1.7) \cdot 10^{-3}T/K, \]  
(19)

\[ \Delta_rG_{AgInSe_2}(T)/(kJ\cdot mol^{-1}) = -(848.8 \pm 10.9) + (96.5 \pm 1.6) \cdot 10^{-3}T/K, \]  
(20)

\[ \Delta_rG_{AgInSe_3}(T)/(kJ\cdot mol^{-1}) = -(224.7 \pm 4.3) + (12.7 \pm 0.3) \cdot 10^{-3}T/K. \]  
(21)

| Phase | -\( \Delta_rG^\circ \) (kJ mol\(^{-1}\)) | -\( \Delta_rH^\circ \) (kJ mol\(^{-1}\)) | \( S^\circ \) (J mol\(^{-1}\) K\(^{-1}\)) |
|-------|---------------------------------|---------------------------------|---------------------------------|
| Ag    | 0                              | 0                              | 42.677                          |
| In    | 0                              | 0                              | 57.823                          |
| Se    | 0                              | 0                              | 42.258                          |
| InSe  | 112.475                        | 117.989                        | 81.588                          |
| In\(_2\)Se\(_3\) | 314.077                        | 326.352                        | 201.25                          |
| In\(_2\)Se\(_3\) (IV) | 943.2±9.4                     | 973.0±11.3                     | 542.8±9.2                       |
| AgIn\(_{11}\)Se\(_{17}\) (I) | 1762.6±18.0                   | 1827.8±20.3                    | 1178.3±16.2                     |
| AgInSe\(_2\) (III) | 190.7±2.1                     | 193.6±3.2                     | 175.3±4.1                      |
| AgInSe\(_2\) (VI) | 220.9±2.8                     | 224.7±4.3                     | 172.3±3.9                      |
| AgInSe\(_3\) (II) | 819.6±8.9                     | 847.2±10.7                    | 577.3±9.8                      |
| AgInSe\(_3\) (V) | 820.0±8.9                     | 848.8±10.9                    | 573.3±9.7                      |

**Table 3.** Values of standard thermodynamic functions of selected compounds of the Ag–In–Se system at T=298 K
Conclusions

The phase composition and triangulation of the equilibrium T-x space of the Ag-In-Se system in the part of AgInSe2-InSe-Se below 500 K have been established. The AgInSe2-InSe-Se concentration space contains seven three-phase regions formed by the InSe, In8Se9, In11Se12, AgInSe2, AgInSe3, and AgIn11Se17 compounds. Equations of the temperature dependences of the Gibbs energy as well as the values of standard thermodynamic functions of the In8Se9, AgInSe2, AgInSe3, and AgIn11Se17 compounds were established for the first time. The phase composition of the InSe–AgInSe2–In5Se7, In8Se9–AgIn11Se17, In11Se12–AgIn11Se17, In17Se25–AgIn11Se17, and AgIn11Se17–AgIn5Se7–Se regions is a combination of stochiometric compounds.

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Термодинамические свойства оксидных сплавов системы Ag–In–Se, вычисленные методом электрокрасочниковых сил

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Рівняважний T–х простір системи Ag–In–Se в частині AgInSe₂–In₂Se₃–Se від 7500 К містить сім трифазних ділянок: In₇Se₈–AgIn₃Se₁₀–In₂Se₃–Se (I), AgIn₃Se₁₀–AgIn₃Se₁₀–Se (II), AgIn₃Se₁₀–AgIn₃Se₁₀–Se (III), In₇Se₈–In₇Se₈–AgIn₃Se₁₀ (IV), In₇Se₈–AgIn₃Se₁₀–In₇Se₈ (V), In₇Se₈–AgIn₃Se₁₀–In₇Se₈ (V), In₇Se₈–AgIn₃Se₁₀–In₇Se₈ (VI). Триангуляція AgInSe₂–In₂Se₃–Se встановлена за температурними залежностями EPC шести електрохімічних комірок (ЕХК) структур: (–)C | Ag | SE | R(Ag⁺) | PE | C (+), де C – інертний електрод (графіт), Ag – негативний (лівий) електрод ЕХК, SE – твердий електроліт (скло Ag₃Ge₅S₇Br), PE – позитивний (правий) електрод ЕХК, R(Ag⁺) – ділянка PE, що контактует з SE, де за участю іонів Ag⁺, як малах центрів зарядження рівняважних фаз, відбувається перебудова фазово нерівноважної суміші сполук ПЕ зазначених в (I)–(VI) в термодинамічно стабільні суміші фаз. За температурними залежностями EPC комірок (E=ф(T) с ПЕ ділянок (I)–(VI) розраховано значення основних термодинамічних функцій бінарної In₇Se₈ та тернарних сплаву у межах фазових ділянках за стандартних умов. Співвідношення значень енергії Гіббса утворення сполук AgIn₃Se₁₀ ΔG°(I)=819.6 ± 8.9 кДж·моль⁻¹ та ΔG°(II)=280.0 ± 8.9 кДж·моль⁻¹ розраховані за E=ф(T) с ПЕ ділянок (I), (V) характеризують фазовий склад ділянок (I), (II), (IV), (V) за 7500 К як поєднання сполук формулюм складу.

Ключові слова: сірблюмісні сполуки, термодинамічні властивості, фазові рівноваги, енергія Гіббса, метод EPC.

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