Short Communication

Thermodynamic properties of solid solutions in the system Ag$_2$S–Ag$_2$Se

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ABSTRACT

We have summarized experimental data on the phase diagram of the system Ag$_2$S–Ag$_2$Se. Standard thermodynamic functions of four solid solutions in this system have been calculated using the model of regular and subregular solutions: a restricted fcc solid solution γ-Ag$_2$S–Ag$_2$S$_{1-x}$Se$_x$ ($x < 0.3$, $867 < T < 1110$ K) and complete bcc solid solution series along β-Ag$_2$S–Ag$_2$Se, monoclinic solid solution (α) from Ag$_2$S to Ag$_2$S$_{0.4}$Se$_{0.6}$, and orthorhombic solid solution (α) from Ag$_2$S$_{0.3}$Se$_{0.7}$ to the Ag$_2$Se. G^{mix} and S^{mix} have been evaluated using the subregular model for asymmetric solution for the region Ag$_2$S$_{0.4}$Se$_{0.6}$–Ag$_2$S$_{0.3}$Se$_{0.7}$. The thermodynamic data can be used for modeling in complex natural systems and in matters of semiconductor materials.

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1. Introduction

The silver chalcogenides (Ag$_2$Se, Ag$_2$S, Ag$_2$(S,Se)) are characterized by unique properties: low lattice thermal conductivity, presence of phase transitions and structural phase transformations [1]. Ag$_2$S and Ag$_2$Se belong to the group of semiconductors. Ag$_4$SSe belongs to the group of n-type semiconductors. These compounds can be used for a variety of different purposes. Some of these include the application in construction of thermoelectrical generators, the Hall sensors, superlattices [2,3].

The possible solid solutions between Ag$_2$S and Ag$_2$Se have been debated for a long time [4–7]. In nature, there occur three minerals of silver with sulfur and selenium: acanthite (α-Ag$_2$S), naumannite (α-Ag$_2$Se) and aguilarite (α-Ag$_4$SeS) [http://www.mindat.org]. The data on the chemical composition of acanthite indicate high selenium impurities, naumannite contains considerable impurities of sulfur, and deviations of sulfur and selenium in relation to Ag$_4$SSe stoichiometry are typical of aguilarite [4–7]. Petruk et al. [5] investigated the relationships between acanthite, aguilarite and naumannite and suggested the compositional limits for these minerals: Ag$_2$S–Ag$_2$S$_{0.85}$Se$_{0.15}$, Ag$_4$S$_{0.95}$Se$_{1.05}$–Ag$_4$S$_{1.10}$Se$_{0.90}$ and Ag$_2$S$_{0.12}$Se$_{0.88}$–Ag$_2$Se. The available experimental data for the

system Ag$_2$S–Ag$_2$Se indicate the presence of two solid solutions at ambient temperatures [7–9]. Sulfur-selenium isomorphous substitution and morphotropic transition in the Ag$_3$Au(Se,S)$_2$ series have been revealed recently by Seryotkin et al. [10].

The thermodynamic characteristics of Ag$_2$S and Ag$_2$Se were studied by many authors and are given in references [11–13]. Thermodynamic properties of solid solutions in the system Ag$_2$S–Ag$_2$Se are lacking in the literature, which does not allow carrying out thermodynamic modeling of either ore-forming or technological processes involving silver sulfoselenides Ag$_2$(S,Se). The aim of this paper is to summarize experimental data and identify areas of the existence of solid solutions in the system Ag$_2$S–Ag$_2$Se, and evaluate their standard thermodynamic functions.

2. Experimental information

The main experimental methods for the study of solid solutions are the diffraction methods, methods of measuring the density and the temperatures of phase transitions and others. Phase diagram of Ag$_2$S–Ag$_2$Se, phase equilibria and solid solutions in this system were investigated in several experimental studies [7–9,14,15]. There are some discrepancies between the results obtained in these studies (Fig. 1). Bontschewa-Mladenowa and Zaneva [14] investigated the system Ag$_2$S–Ag$_2$Se within the composition interval from 0 to 100% in steps of 5 mol.% Ag$_2$Se by differential thermal analysis (DTA), X-ray diffraction and microstructural analysis with additional investigations of the density and microhardness. They found that the phase diagram of this system is characterized by

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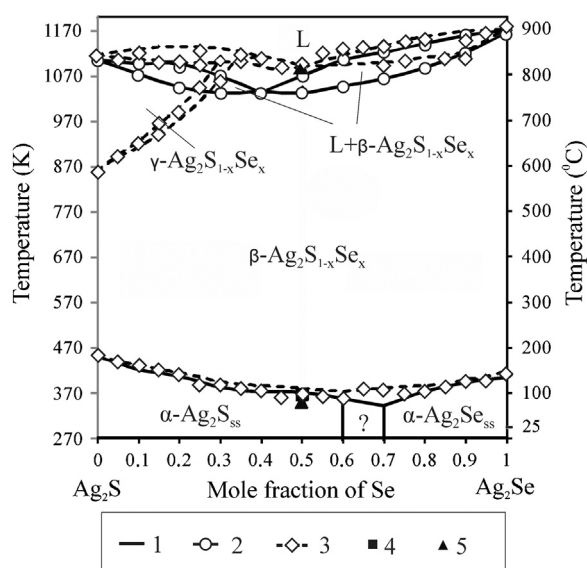
Fig. 1. Phase diagram of the Ag₂S–Ag₂Se system constructed using data from: 1 – [9], 2 – [15], 3 – [14], 4 – [27], 5 – [26].

eutectic (50 mol.% Ag_2Se) and peritectic points (40 mol.% Ag_2Se) at 835 °C, and two continuous solid solutions with a miscibility gap at 50 mol. % Ag_2S (i.e. $Ag_2S_{0.5}Se_{0.5}$ or Ag_4SSe) exist at temperatures below the melting point (T_{melt}). Glazov et al. [15] used DTA to study silver sulfoselenides synthesized in 10 mol. %. They showed that phase equilibriums between the high-temperature modifications in the Ag_2S–Ag_2Se diagrams are described by the continuous series of solid and liquid solutions in the presence of a common minimum point at 760 °C and 40 mol. % Ag_2Se. According to these authors the studied system is well described in terms of a strictly regular approximation.

Pingitore et al. and Ponce [7,8] studied silver sulfoselenides of compositions, ranging from Ag_2S to Ag_2Se, by optical microscopy, electron-probe microanalysis and X-ray diffraction and concluded that there are two solid solutions at ambient conditions. One series extending from Ag_2S to approximately $Ag_2S_{0.4}Se_{0.6}$ is monoclinic. The second series ranging from $Ag_2S_{0.3}Se_{0.7}$ to Ag_2Se is orthorhombic. Calorimetric studies performed by Pingitore et al. [9] confirmed the continuous character of each solid solution. The transition temperature (T_{trans}) depends on the composition of $Ag_2(S,Se)$ solid solutions and varies from 70 to 178 °C with the lowest transition temperatures for phases of $Ag_2S_{0.4}Se_{0.6}$ to $Ag_2S_{0.3}Se_{0.7}$. Determination of the entropy of the transitions was consistent with the model of two solid solutions. The high-temperature allotrope is presumably a continuous solid solution between Ag_2S and Ag_2Se, which have similar body centered cubic (bcc) structures [9]. According to data [6], the field of $Ag_2S_{0.4}Se_{0.6}$–$Ag_2S_{0.3}Se_{0.7}$ at temperatures below T_{trans} is a miscibility gap and "establishment of the precise boundaries of this gap, and likewise of the end members of the two solid solutions, was not possible from available diffraction data". Until it is unclear what can be there: two phase region or solid solution based on any compound.

Petruk et al. [5] described limited formation of solid solutions about these three phases in natural samples (from Ag_2S to $Ag_2S_{0.85}Se_{0.15}$, from $Ag_4S_{1.1}Se_{0.9}$ (or $Ag_2S_{0.55}Se_{0.45}$) to $Ag_4S_{0.95}Se_{1.05}$ (or $Ag_2S_{0.48}Se_{0.52}$), and from $Ag_2S_{0.12}Se_{0.88}$ to Ag_2Se. These authors constructed a speculative phase diagram for the Ag_2S–Ag_2Se system on the basis of a limited number of data on the chemical composition of natural silver sulfoselenides: Se-containing acanthite, aguilarite, S-containing naumannite. Experimental studies carried out later [7–9,16] did not confirm the compositional limits suggested for these minerals.

Structural characteristics of the Ag_2S and Ag_2Se polymorphs have been investigated in several studies [15–21]. There are three polymorphs of Ag_2S [17–19]. Monoclinic acanthite α-Ag_2S is stable up to 176 °C (space group $P2_1/n$). The cubic crystal phases β-Ag_2S (argentite, space group $Im3m$, bcc) and γ-Ag_2S (fcc) are stable in the intervals of 176–592 °C and 592–837 °C. Structural studies of the low-temperature form Ag_2Se have been reported in [21] (X-ray data), [22] (synchrotron data) and [23] (single-crystal data). The structure of α-Ag_2Se is orthorhombic, space group is $P2_12_12_1$. The structure of the high-temperature form of β-Ag_2Se is cubic (space group $Im3m$, bcc) [21]. Aguilarite is definitively proved to be isostructural with acanthite [8,16]. The mineral was found to be monoclinic, crystallizing in space group $P2_1/n$, with $a = 4.2478(2)$, $b = 6.9432(3)$ and $c = 8.0042(5)$ Å, $\beta = 100.103(2)°$, $V = 232.41(2)$ Å³ and $Z = 4$ [16].

Fig. 1 shows a phase diagram based on the experimental data from [7–9,14,15], corrected for data on the transition and melting temperatures for silver sulfoselenide Ag_4SSe. The transition temperature for Ag_2S was determined very accurately 173–179 °C [17,20], for Ag_2Se – 128–133 °C [18,24,25]. Roy et al. [25] showed a slight reduction in the phase transition temperature with increasing pressure to α-Ag_2S to 181 °C and α-Ag_2Se – up to 136 °C at 1100–1200 bar. The temperature of phase transformations for phase Ag_4SSe (aguilarite) was identified in several studies and covers a range of 70–100 °C: <100 ± 5 [14], 94 [26], 75 [27] and 70 °C [9]. The divergence between the data [14] and [15] in the temperature range 750–900 °C in the phase diagram is attributed to the absence of thermal analysis data taken during cooling of the synthesized samples in the second cited work, which led to the error in determining the temperature of thermal effects. Such errors in determining the DSC melting peak was shown in [28]. Diffuse phase transition characteristics of semiconductors were also noted by Aliev [1].

Thus, according to the available experimental data, in the Ag_2S–Ag_2Se system there are a restricted fc and complete bc cubic solid solution series at temperatures below T_{melt} (for Ag_2S: 837 °C, Ag_2Se: 897 °C, Ag_4SSe: 815 °C) [15], and two solid solutions (monoclinic and orthorhombic) with a miscibility gap in the composition between $Ag_2S_{0.4}Se_{0.6}$ and $Ag_2S_{0.3}Se_{0.7}$ at temperatures below T_{trans} (Ag_2S: 176 °C, Ag_2Se: 128 °C, Ag_4SSe – 75 °C). The presence of a solid solution in the above range is possible. Diagram Ag_2S–Ag_2Se can be attributed to the type of diagrams with continuous solid solutions having a minimum at liquidus curve [29] and undergoing a polymorphic transition with the formation of two solid solutions with different crystalline structures at temperatures below 75–176 °C depending on the composition.

3. Model description

The various mixing models that have been used in the treatment of experimental data on mineral solid solutions have been summarized in [29,30]. Models of regular and subregular solid solutions are most appropriate for the study of the Ag_2S–Ag_2Se system.

Glazov et al. [15] estimated the energy of mixing in the system Ag_2S–Ag_2Se for solid (10.1 kJ/mol) and liquid (−4.9 kJ/mol) phases in the temperature range of 750–1200 °C and showed its consistency and the persistence of inequalities $-2RT < G < 2RT$, indicating the formation of regular solutions with unlimited solubility in solid and liquid states. Since the high-temperature modification of $Ag_2(S,Se)$ are described by phase diagrams with a common minimum point on the liquidus and solidus curves, for the evaluation of standard thermodynamic properties in the region of existence of this solution we used the subregular solution model (for symmetric solutions) previously applied to the example of the system Au–Hg [31]. However, calculations of the free energy of mixing

for different compositions of the solid solution $Ag_2(S,Se)$ using the model of continuous solid solution led to positive values that contradict the conditions of their stability, so we had to abandon this model and accepted that a cubic solid solution is continuous and has some differences in the regions of Ag_2S–$Ag_2S_{0.5}Se_{0.5}$ (bcc) and $Ag_2S_{0.5}Se_{0.5}$–Ag_2Se (bcc), in accordance with the results of [14].

Evaluation of standard thermodynamic properties of silver sulfoselenides of low-temperature modifications – two continuous solid solutions of Ag_2S to $Ag_2S_{0.4}Se_{0.6}$ (monoclinic) and $Ag_2S_{0.3}Se_{0.7}$ to the Ag_2Se (orthorhombic) with a gap of miscibility in $Ag_2S_{0.4}Se_{0.6}$ – $Ag_2S_{0.3}Se_{0.7}$ was performed following the model of regular and subregular solutions (for asymmetric solutions).

Table 1 shows the standard thermodynamic properties of the Ag_2S and Ag_2Se phases, as well as space groups and phase transformation temperatures, and the references cited in the original literature [11–13,32–37]. Variations of G^0, H^0 and S^0 values, according to different sources, lie within the range of determination errors of these values obtained using different methods. In the calculations we used the standard thermodynamic characteristics of low-temperature polymorphs of Ag_2S and Ag_2Se from [11,13], high-temperature polymorphs of β, γ-Ag_2S from [11,13], G^0, H^0 and S^0 for β-Ag_2Se are taken from [35], and coefficients a_1 and a_2 in the equation of heat capacity are borrowed from [33]. Molar volumes of α, β, γ-Ag_2S and α, β-Ag_2Se are taken from [11]. The standard entropy values of elementary solid substances Ag, S and Se are taken from [38].

3.1. *Methodology for evaluation of the standard thermodynamic properties of the solid solution $Ag_2(S,Se)$ by the subregular solution model (for symmetric solution)*

The Gibbs energy of one mole of pseudo binary solid solution $Ag_2(S,Se)$ at the pressure of 1 bar and temperature T was calculated by the equation:

$$G_T^0(x_1, x_2) = G^{mix} + x_1 G_1^0 + x_2 G_2^0, \tag{1}$$

where x_1, x_2 is the atomic fraction of sulfur and selenium in solid solution $Ag_2S_{x_1}Se_{x_2}$, $x_2 = 1 - x_1$; $G_0^T(x_1, x_2)$ is the standard Gibbs free energy of the solid solution $Ag_2S_{x_1}Se_{x_2}$; G^{mix} is the free energy of mixing; G_1^0 and G_2^0 are the Gibbs energies of the extreme compositions of solid solution Ag_2S and Ag_2Se under standard conditions [39]. The free energy of mixing was calculated by the equation:

$$G^{mix} = G^{id} + G^{ex}, \tag{2}$$

where $G^{id} = RT(x_1 \ln x_1 + x_2 \ln x_2)$ is the ideal energy of mixing; $G^{ex} = x_1 G_1^{ex} + x_2 G_2^{ex}$ is the excess Gibbs energy of mixing, G_1^{ex}, G_2^{ex} are the partial excess Gibbs energies of the solution components.

The partial excess Gibbs energy of components was calculated using the method of Redlich–Kister [40]:

$$G^{ex} = x_1 x_2 \sum_{k=0}^{n} {}^kL(x_1 - x_2)^k \tag{3}$$

where ${}^kL$ are the parameters of the approximating polynomial. When using this method in calculations, a sufficient degree of accuracy for practical use is achieved by using only two first approximation coefficients:

$$G^{ex} = x_1 x_2({}^0L + {}^1L(x_1 - x_2)) \tag{4}$$

where ${}^0L$ is the parameter of the regular solution, ${}^1L$ is the parameter of subregular solution. Table 2 shows the calculated values of the parameters of regular and subregular solutions for each range of their existence, depending on temperature. The excess partial Gibbs energies were calculated using the finite equations [41]:

$$G_1^{ex} = x_2^2({}^0L + {}^1L(3x_1 - x_2)), \tag{5}$$

$$G_1^{ex} = x_2^2({}^0L + {}^1L(x_1 - 3x_2)), \tag{6}$$

Parameters ${}^0L$ and ${}^1L$ were found by substituting G_1^{ex} and G_2^{ex} from (5) and (6) in the Eqs. (7) and (8) [41]:

$$RT \ln(x_1') + G_1^{ex'} = RT \ln(x_1'') + G_1^{ex''} \tag{7}$$

$$RT \ln(x_2') + G_2^{ex'} = RT \ln(x_2'') + G_2^{ex''} \tag{8}$$

where $G_1^{ex'}$, $G_2^{ex'}$, $G_1^{ex''}$, $G_2^{ex''}$ are the partial excess Gibbs energies of components of solid solutions Ag_2S–$Ag_2S_{0.5}Se_{0.5}$ and $Ag_2S_{0.5}Se_{0.5}$–Ag_2Se and also Ag_2S–$Ag_2S_{0.4}Se_{0.6}$ and $Ag_2S_{0.3}Se_{0.7}$–Ag_2Se, containing x_1' and x_1'' atomic fraction of sulfur and x_2' and x_2'' atomic fraction of selenium, respectively. Atomic fractions of selenium were calculated as $x_2' = 1 - x_1'$, $x_2'' = 1 - x_1''$.

For calculations in the high-temperature region in the range of Ag_2S–$Ag_2S_{0.5}Se_{0.5}$ in Eqs. (7) and (8) the amount of sulfur was defined as follows: $x_1' = 0.99$, $x_1'' = 0.5$, for a range of $Ag_2S_{0.5}Se_{0.5}$–Ag_2Se – $x_1' = 0.5$, $x_1'' = 0.01$. For the low-temperature region we used $x_1' = 0.99$, $x_1'' = 0.4$ in the range of Ag_2S–$Ag_2S_{0.4}Se_{0.6}$, and $x_1' = 0.3$, $x_1'' = 0.01$ in the range of $Ag_2S_{0.3}Se_{0.7}$–Ag_2Se. Atomic fractions of selenium were calculated as $x_2' = 1 - x_1'$, $x_2'' = 1 - x_1''$. The specified procedure requires a linear dependence of parameters ${}^0L$ and ${}^1L$ on temperature, which has the form ${}^iL = a_i RT$, where a_i is the coefficient associated with the composition of the extreme phases at ranges, $i = 1,2$.

To calculate the thermodynamic characteristics of restricted fcc solid solution γ-Ag_2S-$Ag_2S_{1-x}Se_x$ ($x < 0.3$, $867 < T < 1110$ K) (temperature ranges of the existence of γ-phases of solid solution were taken from [12]), γ-Ag_2S and β-$Ag_2S_{0.7}Se_{0.3}$, were taken as the end members of solution and, hence, $x_1' = 0.99$ and $x_1'' = 0.7$ were used for Eqs. (7) and (8).

The standard entropies of the solid solution $Ag_2S_{x_1}Se_{x_2}$ were calculated by the equation:

$$S_T^0 = S^{mix} + x_1 S_1^0 + x_2 S_2^0 \tag{9}$$

where $S^{mix} = S^{id} + S^{ex}$ is the entropy of mixing of the solid solution, $S^{id} = -R(x_1 \ln x_1 + x_2 \ln x_2)$ is the ideal entropy of mixing, S_{ex} is the excess entropy of mixing, S_1^0 and S_2^0 is the standard entropy of extreme compositions of the solid solution – Ag_2S and Ag_2Se. Excess entropy of mixing was estimated using the equation that determines the temperature dependence of the free energy of mixing for each given composition of the solid solution at $p = const$:

$$S^{ex} = -\left(\frac{\partial G^{ex}}{\partial T}\right)_P. \tag{10}$$

Enthalpy of the solid solution $Ag_2S_{x_1}Se_{x_2}$ was found by the equation:

$$\Delta_f H^0 = \Delta_f G^0 + T(S_T^0 - L_T) \tag{11}$$

where $L_T = \sum_j S_j^0 \cdot \frac{x_j}{a_j}$, S_j^0 is the entropy of elementary substances, which consists of a solid solution compound, at the pressure of 1 bar and temperature T, x_j is the atomic fraction of elementary substance in compound formula, a_j is the number of atoms of a elementary substance.

The calculation of the temperature dependence of heat capacity was carried out on the basis of 2-coefficient equation because for the extreme compositions of the system Ag_2S–Ag_2Se only coefficients a_1 and a_2 were identified:

$$Cp = a_1 + a_2 T + \ldots \tag{12}$$

where C_p is the specific heat capacity of a solid solution $Ag_2(S,Se)$, T is the temperature in K for which the dependence was calculated. The standard Gibbs energy of solid solution $Ag_2(S,Se)$ is linearly

Table 1
Standard thermodynamic properties (298.15 K, 1 bar) and space groups of Ag_2S and Ag_2Se phases.

Phase (formula, name, T range)	$\Delta_f G^0$, kJ/mol	ΔH^0, kJ/mol	S^0, J/(mol·K)	V^0, cm³/mol	$C_p = a_1 + a_2\,T + a_3\,T^{-2}$, J/(mol K)			Space groups	Ref.
					a_1	$a_2 \times 10^3$	$a_3 \times 10^{-5}$		
α-Ag_2S	−40.67	−32.59	144.01	**34.2 ± 0.2**	42.38	110.46	–	$P2_1/n$	[11]
acanthite	−39.42	−29.39	150.49	34.19 ± 0.04	75.31	–	–		[32]
298–452 K	−39.7 ± 1.0	−32.0 ± 1.0	142.9 ± 0.3	-	64.60	39.96	–		[12]
	−39.44	**−31.59**	**143.51**				–		[13]
β-Ag_2S	−39.54	−29.41	150.62	**34.8 ± 0.2**	90.54	–	–	$Im3m$	[11]
argentite	−39.71	−32.01	142.88	34.19	75.31	–	–	bcc	[12]
452–895 K	−40.64	−32.56	143.89	–	–	–	–		[32]
	−38.10	**−27.62**	**152.32**		81.34	2.93	–		[13]
γ-Ag_2S	**−37.77**	**-27.12**	**152.88**	–	**82.72**	–	–	fcc	[13]
Silver sulfide	–	–	–	**37.1 ± 0.2**	–	–	–		[11]
895–1115 K									
α-Ag_2Se	**−51.04**	**−44.35**	**150.71**	**36.02**	**64.22**	**65.18**			[11]
naumannite 298–406 K	−46.9	−40.13	149.9	37.50	27.63	125.63	14.55	$P2_12_12_1$	[33]
	−50.2	−43.5	150.17	–	65.15	54.9	–		[34]
	−49.43	−42.69	149.86	–	–	–	–		[35]
	−48.98	−40.58	155.406	–	–	–	–		[36]
	−49.37	−42.32	150.90	–	–	–	–		[37]
β-Ag_2Se	–	–	–	**37.5 ± 0.2**	85.35	-	–	$Im3m$	[11]
Silver selenide	–	−32.47	–	–	**82.44**	**7.0**	–	bcc	[33]
406–1170 K	**−47.39**	**−34.99**	**168.87**	–	-	-	–		[35]
	−47.48	−34.97	169.23	–	-	-	–		[36]
406–1000 K	−47.44	−35.02	168.94	–	-	-	–		[37]
	–	–	–	–	80.50	9.50	–		[34]

Note: bold, thermodynamic constants used in the calculations.

Table 2
The calculated values of the regular and subregular solutions parameters for each range of compositions of solid solutions in the temperature interval from 298 to 973 K.

Solid solution	From Ag_2S to $Ag_2S_{0.5}Se_{0.5}$					From $Ag_2S_{0.5}Se_{0.5}$ to Ag_2Se				
T (K)	298	373	573	773	973	298	373	573	773	973
^0L	−3505	−4385	−6736	−9087	−11,439	−3508	−4388	−6741	−9094	−11,447
^1L	10,292	12,876	19,780	26,684	33,588	−10,292	−12,876	−19,780	−26,684	−33,588

dependent on T, so the second temperature derivative is zero, then the heat capacity of the solid solution is expressed as a linear combination of heat capacities of the extreme members of the solid solution taking into account their mole fractions in solution, which was earlier shown in the example of the Ag–Au system [42]:

$$Cp^0(Ag_2(s,Se)) = x_1 Cp^0(Ag_2S) + x_2 Cp^0(Ag_2Se) \qquad (13)$$

$$a_1(Ag_2(S,Se)) = x_1 a_1(Ag_2S) + x_2 a_1(Ag_2Se) \qquad (13a)$$

$$a_2(Ag_2(S,Se)) = x_1 a_1(Ag_2S) + x_2 a_1(Ag_2Se) \qquad (13b)$$

Molar volumes of solid solutions $Ag_2(S,Se)$ were calculated according to the Retgers's rule on the basis of molar volumes of the extreme components, which is based on a linear dependence at a constant temperature between the properties of the crystal lattice of a solid solution and the concentration of its separate components:

$$V(Ag_2(S,Se)) = x_1 V(Ag_2S) + x_2 V(Ag_2Se) \qquad (14)$$

where $V(Ag_2(S,Se))$ is the molar volume of the solid solution of $Ag_2(S,Se)$, $V(Ag_2S)$ and $V(Ag_2Se)$ are the molar volumes of the extreme components.

The activity of components in the solid solution was calculated by the equations:

$$a_1 = x_1 \exp\left(\frac{G_1^{ex}}{(RT)}\right) \qquad (15a)$$

$$a_2 = x_2 \exp\left(\frac{G_2^{ex}}{(RT)}\right) \qquad (15b)$$

3.2. An asymmetric model for solid solutions $Ag_2(S,Se)$

For evaluation of the thermodynamic properties of the solid solutions $Ag_2(S,Se)$ at temperatures below T_{trans}, when there are two solid solution – from Ag_2S to $Ag_2S_{0.4}Se_{0.6}$ (monoclinic) and from $Ag_2S_{0.3}Se_{0.7}$ to Ag_2Se (orthorhombic) – we also used a subregular model for asymmetric solution. The parameters ^0L and ^1L were calculated for each solid solution at various temperatures (Table 3) and the thermodynamic functions of mixing G^{mix} and S^{mix} were estimated by Eqs. (2) and (9). For the compositions from $Ag_2S_{0.4}Se_{0.6}$ (monoclinic) to $Ag_2S_{0.3}Se_{0.7}$ (orthorhombic), when the extreme terms have different structures and a miscibility gap or the presence of a narrow region of a solid solution decay are expected, the asymmetric solution model was used. The calculation of the excess Gibbs energy G^{ex} for the range of compositions $Ag_2S_{0.4}Se_{0.6}$–$Ag_2S_{0.3}Se_{0.7}$ was conducted in accordance with the procedure from [43]:

$$G^{ex} = x_1 x_2 (W_{12} x_2 + W_{21} x_1) \qquad (16)$$

Table 3
The calculated values of the regular and subregular solutions parameters for low-temperature modifications phases of two solid solutions in the temperature range of 298–338 K.

Solid solution	From Ag_2S to $Ag_2S_{0.4}Se_{0.6}$			From $Ag_2S_{0.3}Se_{0.7}$ to Ag_2Se		
T (K)	298	318	338	298	318	338
^0L	1752	1868	1986	−29,721	−31,700	−33,694
^1L	7479	7977	8478	−22,133	−23,607	−25,092

Table 4
The calculated values of the interaction parameters for phases of compositions from $Ag_2S_{0.4}Se_{0.6}$ to $Ag_2S_{0.3}Se_{0.7}$ depending on the temperature.

Solid solution	From $Ag_2S_{0.4}Se_{0.6}$ to $Ag_2S_{0.3}Se_{0.7}$		
T (K)	298	318	338
W_{12}	5478	5843	6210
W_{21}	5450	5813	6179

where x_1 and x_2 are the mole fractions of sulfur and selenium, changing from 0.4 to 0.3 and from 0.6 to 0.7, respectively, W_{12} and W_{21} are the interaction parameters. Parameters W_{12} and W_{21} were calculated by solving a system of equations based on the condition of equilibrium between two phases A ($Ag_2S_{0.4}Se_{0.6}$) and B ($Ag_2S_{0.3}Se_{0.7}$):
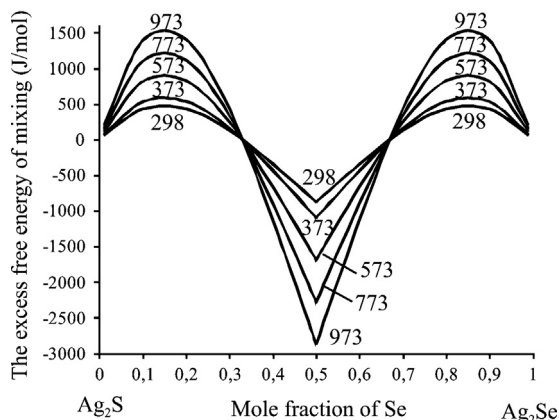
$$RT \ln \left(\frac{x_i^A}{x_i^B} \right) = RT \ln \gamma_i^B - RT \ln \gamma_i^A \qquad (17)$$

where x_i is the atomic fraction of sulfur/selenium in phases A and B, γ_i^A and γ_i^B are the activity coefficients of the components in the phases A and B, respectively; $i = 1, 2$. For binary systems, activity coefficients of the components are equal: $\gamma_i = \exp\{[W_{12}(1 - 2x_i) + 2W_{21}x_i]x_j 2/RT\}$. Values of interaction parameters for low-temperature sulfoselenides of silver with compositions from $Ag_2S_{0.4}Se_{0.6}$ to $Ag_2S_{0.3}Se_{0.7}$ depending on the temperature are shown in Table 4.
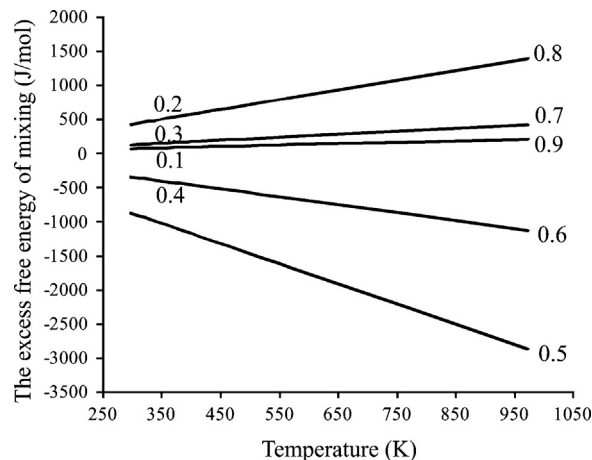
4. Results and discussion

Table 5 shows the calculated thermodynamic properties of high- and low-temperature polymorphs of the solid solution $Ag_2(S,Se)$ with a step x_{Se} 0.1 mole fraction. Excess Gibbs energies of the solid solution $Ag_2(S,Se)$ depending on the composition for different temperatures, calculated by the regular solution model, are shown in Fig. 2. It is shown that the temperature dependence on the composition is symmetric with respect to $Ag_2S_{0.5}Se_{0.5}$. Fig. 3 as an example shows the dependence of the excess Gibbs energy on the temperature at different mole fractions x_{Se}. Lines $x_{Se} = 0.4, 0.3, 0.2, 0.1$ coincide with the lines 0.6, 0.7, 0.8, 0.9, respectively. Free energy of mixing G^{mix} of the solid solution $Ag_2(S,Se)$ depending on the composition is shown in Fig. 4 for the temperature range from 298 to 973 K. The energy of mixing at any composition of a solid solution is negative, indicating that the stability of the solid solution in these conditions

The dependence of the molar volumes of solid solutions on the composition of the low-temperature polymorphs obtained from Eq. (4) and calculated in [16] for the synthesized phases and minerals

(acanthite, aguilarite and naumannite) shows a linear character. Deviations from a straight line, according to [16], are no more than 1 Å^3, which is less than 0.004% of the total cell volume, and confirms the regularity of solid solution $Ag_2(S,Se)$.
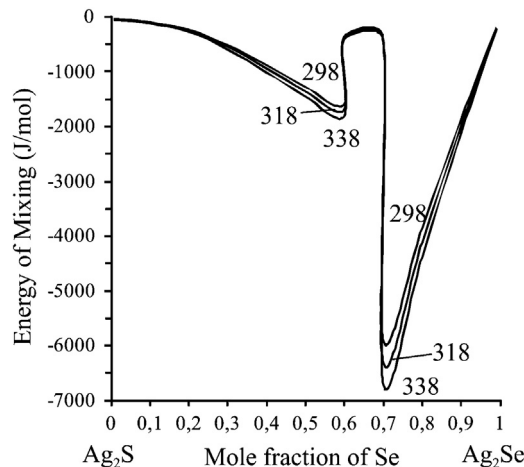
Fig. 3. The excess free energy of mixing of the solid solution $Ag_2(S,Se)$ depending on the temperature at different mole fractions of Ag_2Se.
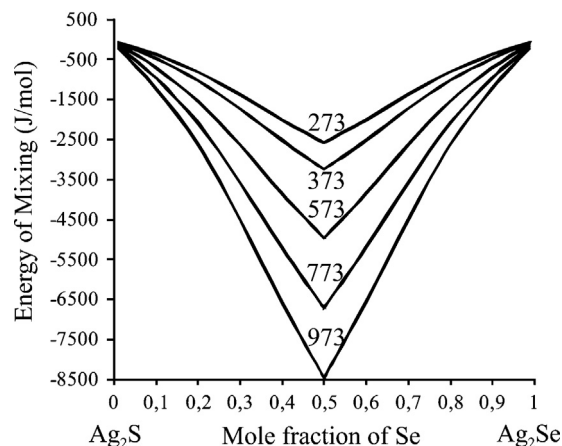
Fig. 4. Free energy of mixing of solid solution $Ag_2(S,Se)$ depending on the composition in the temperature interval from 298 to 973 K.

Fig. 2. The excess free energy of mixing of the solid solution $Ag_2(S,Se)$ depending on the composition at different temperatures.

Fig. 5. The energy of mixing of solid solutions $Ag_2S–Ag_2S_{0.4}Se_{0.6}$ and $Ag_2S_{0.3}Se_{0.7}–Ag_2Se$ in the temperature interval from 298 to 338 K.

Table 5
Thermodynamic properties (298.15 K, 1 bar) a solid solutions of $Ag_2(S,Se)$.

Composition, T range (in K)	$T_{trans}(T_{melt})$	$\Delta_f G^0$, kJ/mol	ΔH^0, kJ/mol	S^0, J/(mol·K)	V^0, cm³/mol	$C_p = a_1 + a_2 T+\ldots$, J/(mol·K)	
						a_1	$a_2 \times 10^3$
α-$Ag_2S_{0.9}Se_{0.1}$ 298–423	423[a]	−40.980	−32.831	145.49	34.38	64.56	42.48
β-$Ag_2S_{0.9}Se_{0.1}$ 423–919	(919)[c]	−39.408	−28.353	155.24	35.07	81.45	3.34
γ-$Ag_2S_{0.9}Se_{0.1}$ 919–1102	(1102)[b]	−38.598	−28.410	155.05	36.95	82.62	–
α-$Ag_2S_{0.8}Se_{0.2}$ 298–413	413[a]	−42.573	−34.074	147.66	34.56	64.52	45.00
β-$Ag_2S_{0.8}Se_{0.2}$ 413–989	(989)[c]	−40.770	−29.086	158.34	35.34	81.56	3.74
γ-$Ag_2S_{0.8}Se_{0.2}$ 989–1099	(1099)[c]	−39.481	−29.368	157.39	36.80	82.51	–
α-$Ag_2S_{0.7}Se_{0.3}$ 298–383	383[a]	−44.306	−35.316	150.29	34.75	64.49	47.53
β-$Ag_2S_{0.7}Se_{0.3}$ 383–1063	(1063)[c]	−42.272	−29.819	161.91	35.61	81.67	4.15
γ-$Ag_2S_{0.7}Se_{0.3}$ 1063–1093	(1093)[c]	−40.504	−30.325	160.21	36.65	82.41	–
α-$Ag_2S_{0.6}Se_{0.4}$ 298–373	373[a]	−46.095	−36.558	153.12	34.93	64.45	50.05
β-$Ag_2S_{0.6}Se_{0.4}$ 373–1033	(1033)[b]	−43.831	−30.551	165.67	35.88	81.78	4.56
α-$Ag_2S_{0.5}Se_{0.5}$ or α-Ag_4SSe 298–367	367[a]	−47.834	−37.790	155.80	35.11	64.41	52.57
β-Ag_4SSe 367–1088	(1088)[b]	−45.339	−31.282	169.26	36.15	81.89	4.97
α-$Ag_2S_{0.4}Se_{0.6}$ 298–358	358[a]	−48.416	−39.031	154.59	35.29	64.37	55.09
β-$Ag_2S_{0.4}Se_{0.6}$ 358–1046	(1046)[b]	−45.690	−32.004	169.01	36.42	82	5.37
α-$Ag_2S_{0.3}Se_{0.7}$ 298–343	343[a]	−48.946	−40.271	153.19	35.47	64.33	57.61
β-$Ag_2S_{0.3}Se_{0.7}$ 343–1063	(1063)[b]	−45.989	−32.735	168.55	36.69	82.11	5.78
α-$Ag_2S_{0.2}Se_{0.8}$ 298–373	373[a]	−49.534	−41.512	151.99	35.66	64.30	60.14
β-$Ag_2S_{0.2}Se_{0.8}$ 373–1087	(1087)[b]	−46.345	−33.465	168.29	36.96	82.22	6.19
α-$Ag_2S_{0.1}Se_{0.9}$ 298–393	393[a]	−50.260	−42.753	151.26	35.84	64.26	62.66
α β-$Ag_2S_{0.1}Se_{0.9}$ 393–1120	(1120)[b]	−46.841	−34.196	168.49	37.23	82.33	6.59

[a] T_{trans} were taken from [9].
[b] T_{melt} were taken from [15].
[c] T_{melt} were taken from [14].

For the asymmetric solution model the thermodynamic functions of mixing G^{mix} and S^{mix} were calculated. The dependence of the energy of mixing of solid solutions Ag_2S–$Ag_2S_{0.4}Se_{0.6}$ and $Ag_2S_{0.3}Se_{0.7}$–Ag_2Se for temperatures in the range of 298–338 K is shown in Fig. 5. The peak on the curve characterizes the miscibility gap or decomposition of solid solution.

5. Conclusions

Four solid solutions: a restricted fcc solid solution γ-Ag_2S-$Ag_2S_{1-x}Se_x$ ($x < 0.3$, $867 < T < 1110$ K), continuous bcc solid solution $Ag_2(S,Se)$, monoclinic Ag_2S-$Ag_2S_{0.4}Se_{0.6}$ and orthorhombic $Ag_2S_{0.3}Se_{0.7}$-Ag_2Se with a miscibility gap in the $Ag_2S_{0.4}Se_{0.6}$–$Ag_2S_{0.3}Se_{0.7}$ were identified by generalizing the published data on the phase diagram of the system Ag_2S–Ag_2Se. The estimation of the standard thermodynamic functions of each solid solution in 0.1 mole fraction x_{Se} was performed. The thermodynamic functions of mixing: G^{mix} and S^{mix} were calculated for a range of compositions $Ag_2S_{0.4}Se_{0.6}$–$Ag_2S_{0.3}Se_{0.7}$. Thermodynamic data can be applied to matters of semiconductor material, as well as for the modeling complex natural systems.

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