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CALCULATION OF STANDARD THERMODYNAMIC FUNCTIONS OF ARGYRODIT Ag_8GeSe_6

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***Abstract** : Based on literature data, with the additional calculations are selected most reliable data for the thermodynamic parameters of crystal silver selenide, germanium and silver selenogermanate: $\Delta H^0_{298}(\alpha\text{-}Ag_2Se)= -43.5$, $\Delta H^0_{298}(GeSe,cr)=-82.9$, $\Delta H^0_{298}(GeSe_2,cr)=-103.7$, $\Delta H^0_{298}(\alpha\text{-}Ag_8GeSe_6,cr)=-290.4$, $\Delta G^0_{298}(\alpha\text{-}Ag_2Se)=-50.3$, $\Delta G^0_{298}(GeSe, cr)=-84.2$, $\Delta G^0_{298}(GeSe_2,cr)= -103.1$, $\Delta G^0_{298}(\alpha\text{-}Ag_8GeSe_6,cr)=-306.3$ $kJ\cdot mol^{-1}$, $S^0_{298}(\alpha\text{-}Ag_2Se)=150.3$, $S^0_{298}(GeSe,cr)=78.3$, $S^0_{298}(GeSe_2, cr)=112.6$, $S^0_{298}(\alpha\text{-}Ag_8GeSe_6, cr)=711.6$ $J\cdot mol^{-1}.K^{-1}$, $C_{p,298}=377.1$ $J\cdot mol^{-1}.K^{-1}$. It was revealed that the compound Ag_2GeSe_3 is formed in the amorphous state, unstable and decomposed into the Ag_8GeSe_6 and $GeSe_2$ compounds. The applicability of the Debye method based on quantum concepts of atomic oscillations in the crystal lattice of a solid in the Magnus-Lindemann and Eastmen-Tsagareishvili approximations for calculating the heat capacity and entropy of a ternary compound with a common chalcogenide anion is revealed.*

***Keywords:** argyrodite Ag_8GeSe_6, thermodynamic functions, Debye method.*
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Introduction

Ag_8GeSe_6 refers to Argurodites with a general chemical formula of A_8BX_6 (A = Cu, Ag; B = Si, Ge, Sn; and X = S, Se, and Te). Some of these compounds, including Ag_8GeSe_6, have ionic conduction and can be used as electrochemical sensors, electrodes and electrolyte materials in solid-state batteries and displays, etc [1-5]. In view of the contradictoriness of the literature data, in [6] phase equilibria in the Ag–Ge–Se system were restudied by differential thermal analysis and X-ray powder diffraction analysis. A number of polythermal sections and an isothermal section at room temperature of the phase diagram were constructed, and so was the projection of the liquids' surface. The primary crystallization fields of phases and types and coordinates of in- and monovariant equilibriums were determined. It showed that a single ternary compound, Ag_8GeSe_6 was formed in the system to have undergone congruent melting at 1175 K and polymorphic transformation at 321 K. The formation of the Ag_2GeSe_3 and Ag_8GeSe_5,compounds previously reported in the literature was not confirmed. Proceeding from phase diagrams of boundary binary systems and the results of the differential thermal analysis of a number of samples of the ternary system, equations were obtained for calculation and 3D modeling of the liquidus Ag_8GeSe_6 [6].

The thermodynamic parameters of the Ag_8GeSe_6 compound are necessary for the development of technology of obtaining the stoichiometric phase from simple substances and from binary compounds. Enthalpy, Gibbs free energy of the formation and entropy of the two Ag_8GeSe_6 modifications as set forth in [7, 8] were carried out within the ternary system study Ag-Ge-Se through measuring the electromotive forces by means of silver solid electrolyte. The results of these studies differ in that the thermodynamic stability of the ternary compound Ag_2GeSe_3 synthesized in [8] was not confirmed in [7]. The isobaric heat capacity of Ag_8GeSe_6, estimated [2] by the Debye method in line with Einstein modules, is not clearly approximated.

Allowing for reasoning stated above, the objective of our work is to analyze

thermodynamic data for Ag_8GeSe_6 argyrodite together with additional thermodynamic calculations based on the Debye method.

Theoretical Part

There are various methods for calculating the thermodynamic parameters of inorganic compounds which have been tested successfully in calculating heat capacity, entropy, enthalpy and Gibbs free energy of the formation of binary and ternary chalcogenides [9-13].

Heat capacity. To calculate the heat capacity, the Debye method is used in keeping with quantum concepts of atomic vibrations in the crystal lattice of a solid. The equation for calculating the isochoric heat capacity Cv for a three-atom compound is as follows [7]:

$$C_v=9R\cdot D(\theta_D/T \quad (1)$$

Where

$$D(\theta_D/T)=12\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^3dx}{e^x-1}-\frac{3\theta_D/T}{e^{(\theta_D/T}-1} \quad (2)$$

and θ_D is the Debye temperature defined as

$$\theta_D=h\nu/k \quad (3)$$

In eqn. (2,3) h is the Planck's constant, k is the Boltzmann constant and ν is the vibrational frequency and the x-parameter is determined on the basis of the solid state theory.

The calculation of the isochoric heat capacity is carried out in the sequence as follows. The initial data provide (Debye) temperatures of the elements forming the compound, as well as the melting points of the elements and compounds below:

$$\theta^*_D=\theta_D(T^{m*}/T^m)^{1/2} \quad (4)$$

Here θ^*_D, θ_D are characteristic temperatures of the element in the compound and the simple substance; T^{m*}, T^m – melting point of the compound and simple substance.

Based on θ^*_D/T function, the values of the isochoric heat capacity (Cv) for each component are found, further summing them up according to the Neumann – Kopp rule, the isochoric heat capacity of the compound is determined. For compounds Ag_8GeSe_6:

$$C_v(Ag_8GeSe_6)=8C_v(Ag)+C_v(Ag)+6C_v(Se) \quad (5)$$

The values of the Debye temperature for silver, germanium, and selenium, together with their melting points and isochoric heat capacities, are given in Table. 1. Recalculation of isochoric heat capacity to isobaric heat was carried out according to the Magnus – Lindemann equation [11]:

$$C_p=C_v+6{,}076\,(nT/T^m)^{3/2} \quad (6)$$

Here n is the number of atoms in the compound. T^m is the melting point of Ag_8GeSe_6. In the equation (3): n=15, T^m=1175 K [6], T=298K.

The temperature dependence of the isobaric heat capacity can be determined by the equation:

$$C_p=a+bT-cT^{-2} \quad (7)$$

$$c=4{,}19\cdot10^5n;\quad b=[25{,}64n+4{,}19\cdot10^5n(T^m)^{-2}-C_{p,298}]/(T^m-298);\quad a=C_{p,298}-298б+4{,}7n \quad (8)$$

Table 1. Melting points (T^m), Debye temperature element in the compound and in a simple substance (θ^*_D, θ_D), isochoric heat capacities and standard entropies of silver, germanium, and selenium.

element	T^m,K	θ_D	θ_D^*	$\theta_D^*/298$	C_v	S^0_{298}
					J· mol^{-1}·K^{-1}	

Ag	1234	221	215.6	0.723	21.31	42.5
Ge	1210	403	397.1	1.332	22.87	31.1
Se	494	90	139.2	0.467	24.67	42.1

As a result of calculations of molar isochoric and isobaric heat capacity of Ag_8GeSe_6, the following values were obtained: $Cv(Ag_8GeSe_6)$ = 365.6 and $C_p(Ag_8GeSe_6)$ = 377.0 $J.mol^{-1}.K^{-1}$.

Entropy. Tsagareishvili [12] extended the range of applicability of the Eastman equation [11] based on the Debye method to obtain the following equation for calculation of standard entropy of inorganic compounds:

$$S_{298}^0 = 0.75nR\left\{\ln\left[\frac{200(M/n)^{5/3}}{\rho^{2/3}T^m}\right]\right\}^{4/3} \quad (9)$$

n = 15- number of atoms in a molecule, R = 8.31 $J.mol^{-1}.K^{-1}$, M = 1410 – molar mass, T^m =1175K [6] – melting temperature, ρ= 6.21 g. sm^{-3} [14] - density Ag_8GeSe_6.

As a result of the calculation, the following value was obtained for the standard entropy $S_{298}^0(Ag_8GeSe_6)$=711.6 $J.mol^{-1}.K^{-1}$.

For the entropy of the formation of compounds from simple substances we have: $\Delta S_{298}^0(Ag_8GeSe_6)$=85.77 $J.mol^{-1}.K^{-1}$.

Enthalpy of compound formation. The value for Ag_8GeSe_6 was determined by calculation based on the data of binary compounds Ag_2Se and $GeSe_2$ (Table 2) in line with a method described in [15,16] with due regard for deviation from additivity ($/\Delta H_{298}^0$):

$$\Delta H_{298}^0(Ag_8GeSe_6,кр) = 4\Delta H_{298}^0(Ag_2Se,кр) + \Delta H_{298}^0(GeSe_2,кр) + /\Delta H_{298}^0 \quad (10)$$

The third term in (10) depends on the number of anion and the binding energy of metal – selenium (Me–Se). In (10): $/\Delta H_{298}^0$ = –6 E(Me–Se), where E(Me–Se)= –2 kC

The free energy of the formation of the Ag_8GeSe_6 compound is calculated using the Gibbs-Helmholtz equation:

$$\Delta G_T^0(Ag_8GeSe_6) = \Delta H_{298}^0(Ag_8GeSe_6) + T\Delta S_{298}^0(Ag_8GeSe_6) \quad (11)$$

as is the case with the formation of (Eq. 10) enthalpy based on the data of binary compounds by the equation:

$$\Delta G_{298}^0(Ag_8GeSe_6,cr) = 4\Delta G_{298}^0(Ag_2Se,cr) + \Delta G_{298}^0(GeSe_2,cr) + /\Delta G_{298}^0 \quad (12)$$

In this work, they also calculated the free energy of the formation of the compound Ag_2GeSe_3, the reliability of which is in doubt. Equation (12) with respect to the compound Ag_2GeSe_3 has the form:

$$\Delta G_{298}^0(Ag_2GeSe_3,cr) = \Delta G_{298}^0(Ag_2Se,cr) + \Delta G_{298}^0(GeSe_2,cr) + /\Delta G_{298}^0 \quad (13)$$

Thermodynamic Calculations and Discussion

The results of the calculation of the thermodynamic parameters of Ag_8GeSe_6 substantially depend on the reliability of these binary compounds Ag_2Se, GeSe and $GeSe_2$. Therefore we analyzed original sources from which the reference data are taken. Thermodynamic data for Ag_2Se and GeSe compounds quoted in various references are consistent with each other [17,18]. At the same time, the enthalpy of the formation of the $GeSe_2$ obtained by different authors [19, 20] significantly differ. The following values were obtained in [19] using the fluorine calorimetry method for the standard enthalpy of the formation of crystalline (cr) and glassy (gl) $GeSe_2$ at 298 K, respectively: $\Delta H_{298}^0(GeSe_2,cr.) = -(103.7 \pm 3.1)$ kJ·mol^{-1} и

$\Delta H^0_{298}(GeSe_2, gl) = -(91.6 \pm 3.2)$ kJ·mol^{-1} . Standard enthalpy of phase transition $GeSe_2(gl) = GeSe_2$ (cr) equals (-12.1 ± 4.2) kJ.mol^{-1}. In [20] while the following values were obtained by the method of direct calorimetry in the standard enthalpy of the formation of crystalline and glassy (amorphous) $GeSe_2$: ΔH^0_{298} ($GeSe_2$,cr) = $-(84.4 \pm 2)$kJ·mol^{-1} and ΔH^0_{298} ($GeSe_2$,gl) = $-(76.5 \pm 1)$ kJ·mol^{-1}. Standard enthalpy of phase transition $GeSe_2$ (gl) → $GeSe_2$ (cr) equals (-7.9 ± 2.1) kJ.mol^{-1}. Value ΔH^0_{298} ($GeSe_2$,cr) = − (62.8 ± 3.1) kJ.mol^{-1}, it seems to be rather understated. The standard entropy values of Ag_2Se, GeSe, and $GeSe_2$ given in various papers [17, 18, 20] gave no rise to doubt. Values S^0_{298} of these compounds are given in Table. 2. Standard free energies of the formation of Ag_8GeSe_6 given in Table. 2 calculated by the Gibbs-Helmholtz equation.

To analyze the dependence of the free energy of the formation of compounds on the composition in Fig. 1, we first calculate the free energy of the reaction:

$$GeSe(cr) + Se\ (cr) \rightarrow GeSe_2(cr) + \Delta G^0_{298} \quad (14)$$

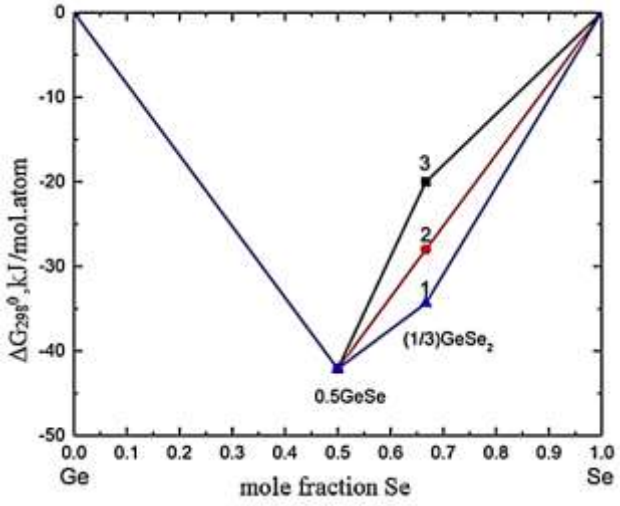

Fig. 1. Dependence of the free energy of formation of selenide and germanium disulfide in the crystalline state on the composition: 1- [19], 2- [20], 3- [18]

According to [19]: $\Delta G^0_{298} = \Delta G^0_{298}(GeSe_2,cr) - \Delta G^0_{298}(GeSe,cr) = -103.7-(-84.2) = -19.5$ kJ.mol^{-1} (Fig. 1, curve 1). According to [8]: ΔG^0_{298} = -83.6-(-84.2 = 0.6 kJ. mol^{-1} (Fig. 1, curve 2). According to [20]: ΔG^0_{298} = -62.8-(-84.2 = 21.4 kJ.mol^{-1} (Fig. 1, curve 3). The last two values for the free energy of reaction (14) are not consistent with reality (Fig.1, curve 2,3). Note that GeSe is a peritectic compound, and $GeSe_2$ is a congruently melting compound.

The results of the calculation of the standard thermodynamic functions of the ternary compound Ag_8GeSe_6, as well as those of Ag_2GeSe_3 are shown in Fig.2. From Fig. 2 it follows that the values $\Delta G^0_{298}(Ag_2GeSe_3)$ given in the work are below additive values that indicate the thermodynamic instability of the Ag_2GeSe_3 compound. In this work, an alloy of this composition was synthesized and investigated. Based on the X-ray diffraction analysis, it revealed that the Ag_2GeSe_3 compound is obtained in the glassy state with rapid cooling of the melt. After annealing of the obtained alloy, there was no line in the XRD diffractogram for the Ag_2GeSe_3 compound. The value of the standard entropy Ag_8GeSe_6, calculated by equation (9), nearly coincides (Table 2) with the results of measuring EMF [7].

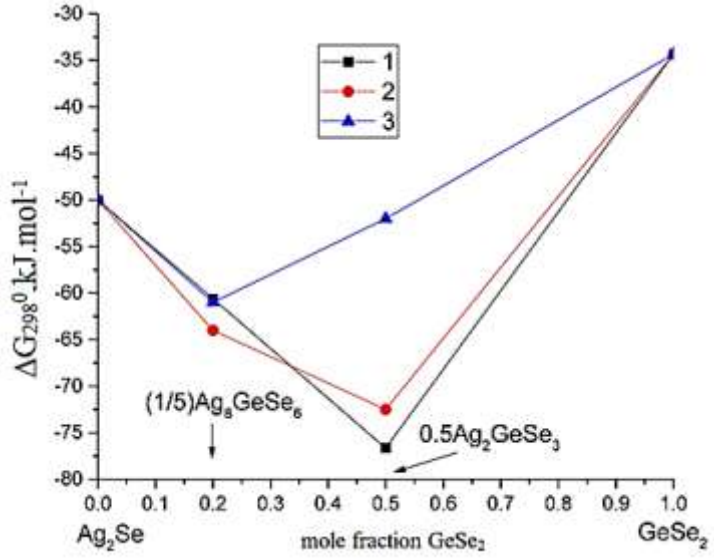

Fig.2. Dependences of the free energy in the formation of ternary compounds in the crystalline state on the composition: 1-additive calculation by Eq. (12.13 with $/\Delta G^0_{298}$ =0), 2-[7], 3-[8].

Table 2. Thermodynamic functions of compounds in the crystalline state

Compound	T,K	$-\Delta G^0_T$	$-\Delta H^0_T$	S^0_{298}	$C_{p,298}$
		kJ.mol^{-1}		J.mol^{-1}.K^{-1}	
α-Ag_2Se	298	50.3±2[18]	43.5±0.5[18]	150.3±1.5[18]	81.8[21]
GeSe	298	84.2±5[18]	82.9±5[18]	78.3±1[18]	50.0[21]
$GeSe_2$	298	103.1±2.0[19]	103.7±3.1 [19]	112.6±2[19]	71.2[21]
α-Ag_8GeSe_6	298	306.3±3[7]	285.7±6[7]	694.1±19[7]	
	298	288.6±5[8]	261.8±5[8]	714.4±10[8]	
	298	316.1±5 calculation by Eq.(12)	290.4±5 calculation by Eq.(10)	711.6±10 calculation by Eq.(9)	377.1 Debye calculation method
β-Ag_8GeSe_6	400	316.6±3[7] 249.0±3[8]	270.7±4[7] 240.9±3[8]	740.9±14[7]	
Ag_8GeSe_6 α→ β	320		15.0±5[7]	46.9±15[7]	

Conclusion

A comparative analysis of the experimental and calculated thermodynamic data for the ternary compound Ag_8GeSe_6 related to Argurodites allowed us to choose the most reliable information about the free energy, formation of enthalpy, standard

entropy, and heat capacity. The work revealed applicability of the Debye method based on quantum concepts of atomic oscillations in the crystal lattice of a solid in the Magnus-Lindemann and Eastmen-Tsagareishvili approximations for calculation of heat capacity and entropy of ternary compound with a common chalcogenide anion.

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References

1. Chekaylo M.V., Ukrainets V.O., Il'chuk G.A., Pavlovskyc Yu.P., Ukrainets N.A.. Differential thermal analysis of Ag–Ge–Se, Ge–Se charge materials in the process of their heating and Ag_8GeSe_6, $GeSe_2$ compound synthesis. *Journal of Non-Crystalline Solids*. 2012, vol. 358, pp.321–327. doi:10.1016/j.jnoncrysol.2011.09.039
2. Xingchen Shen, Chun-Chuen Yang, Yamei Liu, Guiwen Wang, Huan Tan, Yung-Hsiang Tung, Guoyu Wang, Xu Lu, Jian He, and Xiaoyuan Zhou. High-Temperature Structural and Thermoelectric Study of Argyrodite Ag_8GeSe_6. *ACS Appl. Mater. Interfaces*, 2019, vol. 11(2), pp. 2168–2176. DOI: 10.1021/acsami.8b19819
3. Li L., Liu Y., Dai J., Hong A., Zeng M., Yan Z., Xu J., Zhang D., Shan D., Liu Sh. Ren, Z., and Liu J-M. High thermoelectric performance of superionic argyrodite compound Ag_8SnSe_6. *J. Mater. Chem. C.*, 2016, vol. 4, pp. 5806. DOI: 10.1039/c6tc00810k
4. Li, W., Lin, S., Ge, B., Yang, J., Zhang, W., Pei, Y. Low sound velocity contributing to the high thermoelectric performance of Ag_8SnSe_6. *Adv.Sci.*, 2016, vol. 3, p.1600196
5. Semkiv I., Ilchuk H., Pawlowski M., Kusnezh V. Ag_8SnSe_6 argyrodite synthesis and optical properties. *Opto-Electronics Review*, 2017, vol. 25, p. 37.
6. Yusibov Yu.A., Alverdiev I.Dzh., Ibragimova F.S., Mamedov A.N., Tagiev D.B., Babanly M.B. Study and 3D Modeling of the Phase Diagram of the Ag–Ge–Se System. *Russian Journal of Inorganic Chemistry*. 2017, vol. 62, no. 9, pp. 1223–1233. DOI: 10.1134/S0036023617090182
7. Alverdiev Dzh, Bagkheri S.M., Imamalieva S.Z., Yusibova Yu.A. and Babanly M.B. Thermodynamic study of Ag_8GeSe_6 by EMF with an Ag_4RbI_5 solid electrolyte. *Russian Journal of Electrochemistry*. 2017, vol. 53, no. 5, pp. 551–554. DOI: 10.1134/S1023193517050032
8. Moroz M.V. and Prokhorenko M.V. Determination of thermodynamic properties of saturated solid solutions of the Ag–Ge–Se system using EMF technique. *Russ. J.Electrochem*. 2015, vol. 51, no. 7, pp. 697–702. https://doi.org /10.1134 /S1023193515070046
9. Heribert Wiedemeier, Guy Pultz, Umesh Gaur and Bernhard Wunderlich**.** Heat capacity measurements of SnSe and $SnSe_2$. *Thermochimico Acta.* 1981, vol. 43, pp. 297-303.
10. Kurbanova R.D., Mamedov A.N., Alidzhanov A.M., Agdamskaya S.G. System PbTe–$CoSe_2$. *Inorg. Materials.* 2002, no.7, pp. 792-802.
11. Moracheskij A.G., Sladkov I.B. Thermodynamic calculations in metallurgy. Moscow, Metallurgiya Publ., 1985, 136 p. (In Russian).
12. Cagarejshvili D.S. Methods for calculating the thermal and elastic properties of inorganic substances Tbilisi: Mecniereba Publ., 1977, 264 p. (In Georgia).

13. Mamedov A.N., Alieva D.M., Bagirov Z.B., Mamedov V.S. Calculation methods for determining the standard thermodynamic functions of compounds. *Chemical Problems.* 2005, no. 1, pp. 93-96.
14. Otfried Madelung. Semiconductors: Data Handbook. 3rd edition. Springer-Verlag Berlin Heidelberg GmbH. 2004, 690 p. DOI 10.1007/978-3-642-18865-7
15. Mamedov A.N. Thermodynamics of systems with non-molecular compounds: calculation and approximation of thermodynamic functions and phase diagrams. LAP. Germany, 2015, 124 p.
16. Gurbanov G.R., Mamedov Sh.G., Adygezalova M.B. and Mamedov A.N. The $PbSb_2Se_4$–$Pb_5Bi_6Se_{14}$ Section of the Sb_2Se_3–PbSe–Bi_2Se_3 Quasi-Ternary System. *Russian Journal of Inorganic Chemistry*. 2017, vol. 62, no.12, pp. 1659-1664. DOI: 10.1134/S0036023617120099
17. Mamedov A.N., Azhdarova D.S., Ahmedova Dzh.A., Abilov CH.I. Inorganic substances synthesized and studied in Azerbaijan. Reference book. Baku: Elm Publ., 2004, 462 p.
18. Physicochemical fundamentals of semiconductor substances. Directory. Team of authors. Moscow: Nauka Publ., 1978, 339 p. (In Russian)
19. O'Hare P.A.G., Susman S., Volin K.J. The energy difference between the crystalline and vitreous forms of germanium diselenide as determined by combustion calorimetryin fluorine. The Ge-Se bond energy. *J. Non-Crystall. Solids.* 1987, vol. 89, iss. 1-2, pp. 24–30.
20. Boone Steve, Kleppa O.J. Enthalpies of formation for G roup IV selenides (GeSe2,GeSe2(am), SnSe, SnSe2, PbSe) by direct combination drop calorimetry *Thermochimica Acta.* 1992, vol. 197, iss. 1, pp. 109–121.
21. Glushko V.P. Thermal constants of substances. Database. URL: http://www.chem.msu.su/cgi-bin/tkv.pl?show=welcome.html.

Ag_8GeSe_6 ARQİRODİTİN STANDART TERMODİNAMİKİ FUNKSİYALARININ HESABLANMASI

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Nəzəri hesablamalar və ədəbiyyat məlumatlarının təhlili əsasında kristal halı üçün gümüş, germanium selenidləri və gümüş selenogermanatlarının termodinamik parametrlərinin ən etibarlı qiymətləri seçilmişdir: $\Delta H^0_{298}(\alpha\text{-}Ag_2Se) = -43.5$, $\Delta H^0_{298}(GeSe,cr) = -82.9$, $\Delta H^0_{298}(GeSe_2,cr) = -103.7$, $\Delta H^0_{298}(\alpha\text{-}Ag_8GeSe_6,cr) = -290.4$, $\Delta G^0_{298}(\alpha\text{-}Ag_2Se) = -50.3$, $\Delta G^0_{298}(GeSe,cr) = -84.2$, $\Delta G^0_{298}(GeSe_2,cr) = -103.1$, $\Delta G^0_{298}(\alpha\text{-}Ag_8GeSe_6,cr) = -306.3$ $kJ\cdot mol^{-1}$, $S^0_{298}(\alpha\text{-}Ag_2Se) = 150.3$, $S^0_{298}(GeSe,cr) = 78.3$, $S^0_{298}(GeSe_2,cr) = 112.6$, $S^0_{298}(\alpha\text{-}Ag_8GeSe_6,cr) = 711.6$ $J\cdot mol^{-1}.K^{-1}$, $C_{p,298} = 377.1$ $J\cdot mol^{-1}.K^{-1}$. *Amorf halında mövcud olan Ag_2GeSe_3 birləşməsi qeyri-sabit olduğu üçün Ag_8GeSe_6 və $GeSe_2$ birləşmələrinə parçalanır. Ag_8GeSe_6 birləşməsinin misalında müəyyən edildi ki, Magnus-Lindemann və Eastmen-Tsagareishvili yaxınlaşmaları əsasında Debay metodu ümumi xalkogenid anionlu üçlü birləşmənin istilik tutumu və entropiyasını hesablamaq üçün istifadə oluna bilər.*

***Açar sözlər**: argyrodite Ag_8GeSe_6, termodinamiki funksiyalar, Debay metodu*

РАСЧЕТ СТАНДАРТНЫХ ТЕРМОДИНАМИЧЕСКИХ ФУНКЦИЙ АРГИРОДИТА Ag_8GeSe_6

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На основании анализа литературных данных с проведением дополнительных расчетов выбраны наиболее достоверные данные для термодинамических параметров кристаллических селенидов серебра, германия и селеногерманата серебра: $\Delta H^0_{298}(\alpha\text{-}Ag_2Se) = -43.5$, $\Delta H^0_{298}(GeSe,кр) = -82.9$, $\Delta H^0_{298}(GeSe_2,кр) = -103.7$, $\Delta H^0_{298}(\alpha\text{-}Ag_8GeSe_6,кр) = -290.4$, $\Delta G^0_{298}(\alpha\text{-}Ag_2Se) = -50.3$, $\Delta G^0_{298}(GeSe,кр) = -84.2$, $\Delta G^0_{298}(GeSe_2,кр) = -103.1$, $\Delta G^0_{298}(\alpha\text{-}Ag_8GeSe_6,кр) = -306.3$ *kJ·mol*$^{-1}$, $S^0_{298}(\alpha\text{-}Ag_2Se) = 150.3$, $S^0_{298}(GeSe,кр) = 78.3$, $S^0_{298}(GeSe_2,кр) = 112.6$, $S^0_{298}(\alpha\text{-}Ag_8GeSe_6,кр) = 711.6$ *Дж·мол*$^{-1}$*.К*$^{-1}$, $C_{p,298} = 377.1$ *Дж·мол*$^{-1}$*.К*$^{-1}$. *Выявлено, что соединение Ag_2GeSe_3 образуется в аморфном состоянии, неустойчиво и распадается на соединения Ag_8GeSe_6 и $GeSe_2$. Показана применимость метода Дебая, основанного на квантовые представления о колебаниях атомов в кристаллической решетке твердого тела в приближениях Магнуса-Линдемана и Истмена-Цагарейшвили, для расчета теплоемкости и энтропии тройного соединения с общим халькогенид анионом.*

***Ключевые слова**: аргиродит Ag_8GeSe_6, термодинамические функции, метод Дебая*