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Abstract	In this study, the low-temperature synthesis and thermodynamic properties of the $AgGaGeS_4$ compound were analyzed in detail for potential applications in optoelectronics and gas sensors. The existence of two four-phase regions Ge–GeS–Ga_2S_3–$AgGaGeS_4$ and GeS–GeS_2–Ga_2S_3–$AgGaGeS_4$ in the Ge–GeS_2–Ga_2S_3–$AgGaS_2$ part of the Ag–Ga–Ge–S system, which are in equilibrium below (540 ± 5) K, has been confirmed through the modified electromotive force (EMF) method. The spatial position of the four-phase regions relative to the silver point was employed to ascertain the overall potential-forming reactions of the $AgGaGeS_4$ synthesis from mixtures of silver, germanium, and compounds (Ga_2S_3, GeS, GeS_2, $AgGaS_2$) in the positive electrodes of electrochemical cells. Based on the results obtained, the temperature dependences of the EMF of electrochemical cells were used to determine the values of standard thermodynamic functions (Gibbs energy, enthalpy, and entropy) of the $AgGaGeS_4$ compound.

Keywords (separated by '-')	Optoelectronic compounds - Gas sensors - Phase equilibria - Thermodynamic properties - EMF method - Gibbs energy

Low-Temperature Synthesis and Thermodynamic Properties of the $AgGaGeS_4$ Compound for Potential Applications in Optoelectronics and Gas Sensors

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Abstract In this study, the low-temperature synthesis and thermodynamic properties of the $AgGaGeS_4$ compound were analyzed in detail for potential applications in optoelectronics and gas sensors. The existence of two four-phase regions Ge–GeS–Ga_2S_3–$AgGaGeS_4$ and GeS–GeS_2–Ga_2S_3–$AgGaGeS_4$ in the Ge–GeS_2–Ga_2S_3–$AgGaS_2$ part of the Ag–Ga–Ge–S system, which are in equilibrium below (540 ± 5) K, has been confirmed through the modified electromotive force (EMF) method. The spatial position of the four-phase regions relative to the silver point was employed to ascertain the overall potential-forming reactions of the $AgGaGeS_4$

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synthesis from mixtures of silver, germanium, and compounds (Ga_2S_3, GeS, GeS_2, $AgGaS_2$) in the positive electrodes of electrochemical cells. Based on the results obtained, the temperature dependences of the EMF of electrochemical cells were used to determine the values of standard thermodynamic functions (Gibbs energy, enthalpy, and entropy) of the $AgGaGeS_4$ compound.

Keywords Optoelectronic compounds · Gas sensors · Phase equilibria · Thermodynamic properties · EMF method · Gibbs energy

Introduction

The investigation of multinary compounds with unique properties and wide thermal stability ranges provides a foundation for low-carbon technical innovations. Metal chalcogenides have been the subject of considerable interest over the past several decades, largely due to their notable nonlinear optical effect, extensive transparent range, and high resistance to laser damage. These materials are being developed for applications in optoelectronics, gas sensors, photomedicine, free space communications, and other fields. However, the synthesis of effective mid-infrared nonlinear optical metal chalcogenides remains a significant challenge, primarily due to the difficulty in achieving an optimal balance between the nonlinear optical effect and laser damage threshold [1, 2]. The distinctive feature of the crystal structure of complex defective diamond-like semiconductors is the random arrangement of atoms from different chemical elements in specific nodes of the crystal lattice. This results in low thermal conductivity, extensive light transparency, and the emergence of electronic and hole conductivity. These semiconductors are promising materials for applications in electronic, thermoelectric, optoelectronic, and sensor devices [2, 3].

Among the class of multinary sulfides, the thiogermanate $AgGaGeS_4$ (AGGS) is regarded as one of the most promising nonlinear optical materials for the mid-infrared region of the electromagnetic spectrum (0.5–11.5 μm), exhibiting a bandwidth of $E_g = 2.78$ eV [4–8]. Valakh et al. [9] published results of experimental polarized Raman and infrared vibrational spectroscopy of $AgGaGeS_4$ single crystals. The process of $AgGaGenS_{2(n+1)}$ ($n = 2$, 3, 4, and 5) polycrystal synthesis by different experimental methods has been described in detail in Ref. [10]. Stoichiometric AGGS melts congruently at 1136 K and crystallizes in the non-centrosymmetric space group *Fdd*2 with unit cell parameters equal to $a = 1.2028$, $b = 2.2918$, and $c = 0.6874$ nm [3, 11]. The AGGS is a high-resistivity conductor with a specific conductivity of $\sigma = 1.67 \times 10^{-9}\ \Omega^{-1}\ \text{cm}^{-1}$ at 300 K [7]. The compound is distinguished by high double refraction, a substantial laser damage threshold, and the absence of absorption peaks at the wavelengths of solid-phase lasers. The piezoelectric properties of AGGS were found to exhibit a significant enhancement when illuminated by a microsecond CO_2 laser [1]. However, the low manufacturability of crystals represents a significant challenge to the wide application of AGGS [3]. Experimental phase diagrams and reliable thermodynamic data are required for the development of modern preparative methods and the controlled synthesis of novel complex phases and materials based on them [12–16]. To the best of our knowledge, the thermodynamic properties of AGGS have not yet been investigated.

The objective of the present study is to synthesize and determine the standard thermodynamic properties of the $AgGaGeS_4$ compound stable below 600 K. Electronic devices fabricated with the inclusion of AGGS are most likely to be utilized in the temperature range of 300–600 K. The Calphad method can be used to model the equilibrium phase space at $T < 600$ K, both in the Ag–Ga–Ge–S and in more complex five-element systems, by combining the thermodynamic properties of the AGGS compound and the available equilibrium phase diagrams data [17–20].

Experimental

For the present investigation, the elemental substances Ag, Ga, Ge, and S of purity greater than 99.9% from Alfa Aesar (Germany) were used for the synthesis of the $AgGaGeS_4$, $AgGaS_2$, Ga_2S_3, GeS, and GeS_2 compounds. The evacuated melts of compounds, cooled to room temperature, were crushed to a particle size of approximately (1.0 ± 0.1) µm and subsequently analyzed for their phase composition via X-ray diffraction (XRD). The STOE STADI P diffractometer, equipped with a linear position-sensitive detector, in a Guinier geometry (transmission mode, $CuK\alpha_1$ radiation, a bent Ge(111) monochromator, and $2\theta/\omega$ scan mode) was utilized for these investigations. The following software programs were employed for the analysis of the obtained results: STOE WinXPOW [21], PowderCell [22], FullProf [23], and crystal structure databases [24, 25].

According to the results of XRD analysis, the sample with nominal composition $AgGaGeS_4$ is a single-phase sample (Fig. 1) and contains $AgGaGeS_4$ compound: own structure type, space group $Fdd2$, $Z = 8$, refined unit-cell parameters and volume are $a = 1.20407(5)$, $b = 2.29303(9)$, $c = 0.68741(3)$ nm, $V = 1.89791(13)$ nm^3. Our data are in good agreement with the original work [26] and JCPDS Cards No. 65–7627, 72–1912. Powders from other compounds were used to fabricate the positive electrodes (PEs) of the electrochemical cells (ECs).

The composition of equilibrium phases and the division of the Ge–GeS_2–Ga_2S_3–$AgGaS_2$ part of the Ag–Ga–Ge–S system below 600 K were established by the modified electromotive force (EMF) method [27, 28]. For these investigations, a certain number of ECs were assembled:

$$(-)\mathrm{C}||\mathrm{Ag}||\mathrm{SE}||\mathrm{R(Ag+)}||\mathrm{PE}||\mathrm{C}(+),$$

where C is the graphite (inert electrode), Ag is the left (negative) electrode, SE is the solid-state electrolyte with purely ionic conductivity (Ag_2GeS_3 glass [29, 30]). Previously, the thermodynamic properties of a number of complex silver chalcogenides have been studied by the EMF method using different solid electrolytes in ECs [31, 32]. R(Ag^+) represents the region of PE that contacts with SE. In this region, the

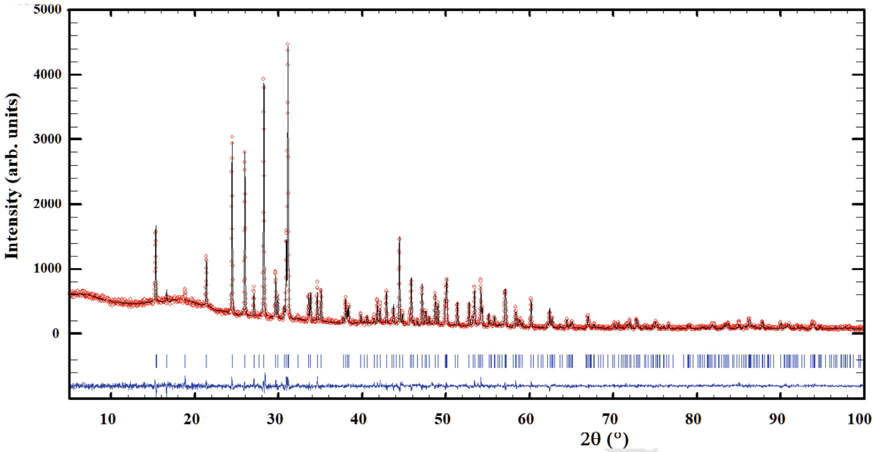

Fig. 1 Observed and calculated X-ray powder diffraction patterns for $AgGaGeS_4$ (Cu $K\alpha_1$-radiation). Experimental data (circles) and calculated profile (solid line through the circles) are presented together with the calculated Bragg positions (vertical ticks) and difference curve (bottom solid line). Reliability factors are $R_P = 0.0615$, $R_{WP} = 0.0831$, $\chi^2 = 1.75$

participation of Ag^+ ions as minor centers of nucleation for equilibrium phases at $T < 540$ K facilitates the rearrangement of non-equilibrium mixtures of compounds into thermodynamically stable mixtures of phases, including the $AgGaGeS_4$ compound. The figurative points of nonequilibrium mixtures of PE compounds covered the entire concentration space of the Ge–GeS_2–Ga_2S_3–$AgGaS_2$.

The experiments were performed in a resistance furnace as previously described in Ref. [33]. To assemble the ECs, a fluoroplastic base with a 2 mm diameter hole was utilized. The powder components of ECs were compressed at a pressure of 10^8 Pa into the hole under a load of (2.0 ± 0.1) tons resulting in a density of $\rho = (0,93 \pm 0,02)\ \rho_0$, where ρ_0 is the experimentally determined density of the cast samples. The assembled cells were placed in a quartz tube with nozzles for the purging of argon gas, as previously described in Ref. [34]. The argon gas flow was directed from the left to the right electrodes of ECs at a rate of (10.0 ± 0.2) $cm^3\ min^{-1}$. The temperature of ECs was maintained by an electronic thermostat with an accuracy ± 0.5 K. A Picotest M3500A digital voltmeter with an input impedance of $> 10^{12}\ \Omega$ was used to measure the EMF (E) values of the cells (accuracy ± 0.3 mV) across a range of temperatures. The synthesis of the equilibrium set of phases in $R(Ag^+)$ region was achieved within 3 days at 500 K. The reproducibility of the E versus T dependences ($E(T)$) of ECs in heating–cooling cycles was a key indicator for the completion of the equilibrium phase formations in the $R(Ag^+)$ region.

Results and Discussion

The triangulation of the Ge–GeS_2–Ga_2S_3–$AgGaS_2$ part of the Ag–Ga–Ge–S system in the vicinity of the $AgGaGeS_4$ compound is shown in Fig. 2.

Two four-phase regions Ge–GeS–Ga_2S_3–$AgGaGeS_4$ (the phase region (I)) and GeS–GeS_2–Ga_2S_3–$AgGaGeS_4$ (phase region (II)) with a common three-phase region GeS–$AgGaGeS_4$–Ga_2S_3 (shaded part of the figure) are highlighted by the lines of two-phase equilibria. For each of the four-phase regions, two basic rules of the EMF method [35] are satisfied:

(1) in the boundaries of a particular phase region, the value of the EMF of EC at a particular temperature is independent of the ratio of equilibrium phases formed in the $R(Ag^+)$;

(2) the phase region more distant from the Ag point at $T = \text{const}$ is characterized by a larger value of the EMF (Table 1 and Fig. 3).

The dependences of $E(T)$ in Fig. 3 intersect at a temperature of 540 ± 5 K. This means that the triangulation variant presented in Fig. 2 above this temperature loses its meaning, since the more distant four-phase region is characterized by a smaller value of EMF. One explanation for the intersection of the two $E(T)$ lines is the decay of the low-temperature modification of $AgGaGeS_4$. This implies the existence of AGGS in two temperature intervals separated by a two-phase region.

The spatial position of the phase regions (I) and (II) relative to the silver point was used to determine the overall potential-forming reactions with the participation of the AGGS compound:

$$2Ag + 5GeS + Ga_2S_3 = 2AgGaGeS_4 + 3Ge, \qquad \text{(R1)}$$

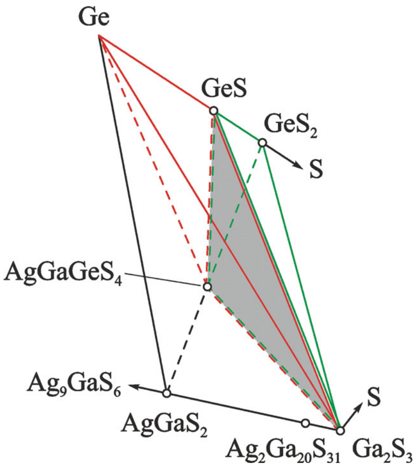

Fig. 2 Triangulation of the Ag–Ga–Ge–S system in the Ge–GeS_2–Ga_2S_3–$AgGaS_2$–Ge part at $T < (540 \pm 5)$ K

Table 1 Measured values of temperature (T) and EMF (E) of the ECs with PE of the phase regions (I) and (II) at pressure $P = 10^5$ Pa. Standard uncertainties u are $u(T) = 0.5$ K, $u(P) = 10^4$ Pa, and $u(E) = 0.3$ mV

T/K	Phase regions		T/K	Phase regions	
	(I)	(II)		(I)	(II)
	$E_{(I)}$/mV	$E_{(II)}$/mV		$E_{(I)}$/mV	$E_{(II)}$/mV
469.9	246.4	256.2	499.4	258.1	264.1
474.8	248.0	257.4	504.3	260.5	265.4
479.8	250.0	258.8	509.2	262.7	267.1
484.7	252.2	260.6	514.2	264.5	268.6
489.6	254.7	261.5	519.0	266.8	269.7
494.5	256.6	263.1	523.9	268.8	271.9

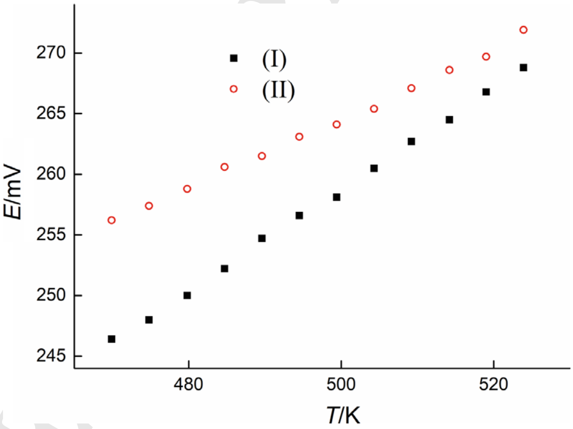

Fig. 3 $E(T)$ dependences of the ECs with PE of the phase regions (I) and (II)

$$2Ag + 3GeS_2 + Ga_2S_3 = 2AgGaGeS_4 + GeS. \quad \text{(R2)}$$

Reactions (R1) and (R2) were carried out in the PE of ECs, the mixture of phases of which corresponds to phase regions (I) and (II), respectively. In accordance with equations (R1), (R2), the ratios of components for the preparing PEs of ECs were determined: 5GeS, Ga_2S_3, $2AgGaGeS_4$, 3Ge and $3GeS_2$, Ga_2S_3, $2AgGaGeS_4$, GeS, respectively. In the above mixture of components, the quaternary compound is represented as a combination of the $AgGaS_2$ and GeS_2 compounds.

The $E(T)$ experimental dependences were processed using the least squares method, as detailed in Refs. [36, 37]. The resulting data are presented in the form of Eq. (1):

$$E = a + bT \pm k_{St}\sqrt{\left(\frac{u_E^2}{f} + u_b^2\left(T - \overline{T}\right)^2\right)}, \quad (1)$$

where a and b are coefficients of linear equation, k_{St} is the Student's parameter [38], f is the number of experimental pairs E_i and T_i, u_E^2 and u_b^2 are the statistical dispersions of the E and b quantities, respectively. The results of calculations are listed in the Table 2.

The Gibbs energy ($\Delta_r G$), enthalpy ($\Delta_r H$), and entropy ($\Delta_r S$) of reactions (R1) and (R2) can be calculated by applying the thermodynamic Eqs. (2)–(4):

$$\Delta_r G = -n \, \mathrm{F} \, E, \tag{2}$$

$$\Delta_r H = -n\mathrm{F} \left[E - \left(\frac{dE}{dT} \right) T \right], \tag{3}$$

$$\Delta_r S = n\mathrm{F} \, (dE/dT), \tag{4}$$

where n is the number of electrons involved in the reactions (R1) and (R2), F is the Faraday's constant, and E is the EMF of the ECs.

The thermodynamic functions of the reactions (R1) and (R2) were calculated using Eqs. (2)–(4) in the standard state ($T = 298$ K and $P = 10^5$ Pa). The results of these calculations are presented in Table 3.

The Gibbs energy, enthalpy, and entropy of reaction (R1) are related to the Gibbs energy, enthalpy, and entropy of compounds and pure substances by Eqs. (5)–(7):

$$\Delta_{r(R1)} G^\circ = 2\Delta_f G^\circ_{\mathrm{AgGaGeS_4}} - 5\Delta_f G^\circ_{\mathrm{GeS}} - \Delta_f G^\circ_{\mathrm{Ga_2S_3}}, \tag{5}$$

$$\Delta_{r(R1)} H^\circ = 2\Delta_f H^\circ_{\mathrm{AgGaGeS_4}} - 5\Delta_f H^\circ_{\mathrm{GeS}} - \Delta_f H^\circ_{\mathrm{Ga_2S_3}}, \tag{6}$$

Table 2 Coefficients and statistical dispersions of the $E(T)$ data of the ECs

Phase regions	$E = a + bT \pm k_{St}\sqrt{\left(\frac{u_E^2}{f} + u_b^2 (T - \overline{T})^2\right)}$
(I)	$E = 49.16 + 419.12 \times 10^{-3} T \pm 2.179\sqrt{\left(\frac{5.36 \times 10^{-2}}{12} + 1.56 \times 10^{-5} (T - 496.9)^2\right)}$
(II)	$E = 123.12 + 282.88 \times 10^{-3} T \pm 2.179\sqrt{\left(\frac{8.06 \times 10^{-2}}{12} + 2.34 \times 10^{-5} (T - 496.9)^2\right)}$

Table 3 Standard thermodynamic data of the reactions (R1) and (R2). Uncertainties for the thermodynamic quantities are standard uncertainties

Reactions	$-\Delta_r G^\circ$	$-\Delta_r H^\circ$	$\Delta_r S^\circ$
	kJ mol $^{-1}$	kJ mol $^{-1}$	J mol $^{-1}$ K $^{-1}$
(R1)	33.59 ± 0.33	9.49 ± 0.43	80.88 ± 1.66
(R2)	40.60 ± 0.41	24.34 ± 1.01	54.59 ± 2.03

$$\Delta_{r(R1)}S^\circ = 2S^\circ_{AgGaGeS_4} + 3S^\circ_{Ge} - 2S^\circ_{Ag} - 5S^\circ_{GeS} - S^\circ_{Ga_2S_3}. \tag{7}$$

It follows from Eqs. (5)–(7) that:

$$\Delta_f G^\circ_{AgGaGeS_4} = 0.5\left(5\Delta_f G^\circ_{GeS} + \Delta_f G^\circ_{Ga_2S_3} + \Delta_{r(R1)}G^\circ\right), \tag{8}$$

$$\Delta_f H^\circ_{AgGaGeS_4} = 0.5\left(5\Delta_f H^\circ_{GeS} + \Delta_f H^\circ_{Ga_2S_3} + \Delta_{r(R1)}H^\circ\right), \tag{9}$$

$$S^\circ_{AgGaGeS_4} = 0.5\left(2S^\circ_{Ag} + 5S^\circ_{GeS} + S^\circ_{Ga_2S_3} - 3S^\circ_{Ge} + \Delta_{r(R1)}S^\circ\right). \tag{10}$$

Similarly to Eqs. (8)–(10), the reactions for determining the thermodynamic functions of the $AgGaGeS_4$ compound by reaction (R2) in phase region (II) were written. Taking into account Eqs. (8)–(10), the literature thermodynamic data of simple substances Ag, Ga, Ge, S and binary compounds GeS, GeS_2, Ga_2S_3 [39], the standard thermodynamic functions of the $AgGaGeS_4$ compound were calculated for the first time. The resulting calculations are presented in Table 4.

From the data in Table 4 it can be seen that the calculated values of the Gibbs energy of the $AgGaGeS_4$ compound in the phase regions (I) and (II) agree within the error of the experiment (relative difference is less than 1%). This confirms:

(1) the phase composition and the partitioning of the concentration space of the Ag–Ga–Ge–S system in the Ge–GeS_2–Ga_2S_3–$AgGaS_2$ part;
(2) the reliability of the calculated values of the thermodynamic functions of the $AgGaGeS_4$ compound.

The temperature dependences of the Gibbs energies of the formation of the $AgGaGeS_4$ compound in the phase regions (I) and (II) are described by equations:

Table 4 Summary of standard thermodynamic data of selected compounds of the Ag–Ga–Ge–S system at 298 K. Uncertainties for $\Delta_f G^\circ$, $\Delta_f H^\circ$, and S° are standard uncertainties

Phases	Phase regions	$-\Delta_f G^\circ$	$-\Delta_f H^\circ$	S°	[Refs.]
		kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}	
Ag	–	0	0	42.677	[39]
Ga	–	0	0	40.828	[39]
Ge	–	0	0	31.087	[39]
S	–	0	0	32.056	[39]
GeS	–	76.995	76.149	65.982	[39]
GeS_2	–	154.588	156.900	87.446	[39]
Ga_2S_3	–	505.702	516.306	142.256	[39]
$AgGaGeS_4$	(I)	462.1 ± 4.8	453.3 ± 7.2	272.6 ± 8.1	This work
$AgGaGeS_4$	(II)	466.5 ± 5.1	467.6 ± 7.5	239.3 ± 7.6	This work

$$\Delta_f G_{\mathrm{AgGaGeS_4,(I)}}/\left(\mathrm{kJ\ mol^{-1}}\right) = -(453.3 \pm 7.2) - (29.7 \pm 0.9)10^{-3}T/\mathrm{K}, \quad (11)$$

$$\Delta_f G_{\mathrm{AgGaGeS_4,(II)}}/\left(\mathrm{kJ\ mol^{-1}}\right) = -(467.6 \pm 7.5) + (3.5 \pm 0.1)10^{-3}T/\mathrm{K}. \quad (12)$$

Conclusions

Low-temperature synthesis of the $AgGaGeS_4$ compound in the positive electrodes of two electrochemical cells, which are initially non-equilibrium mixtures of phases of elemental substances (Ag, Ge) and compounds (Ga_2S_3, GeS, GeS_2, $AgGaS_2$), was carried out. The catalyst for the synthesis was Ag^+ cations acting as small nucleation centers of equilibrium phase mixtures, including the quaternary compound. The temperature dependences of the EMF of two electrochemical cells with different compositions of the equilibrium phase mixtures of the positive electrodes intersect at $T = (540 \pm 5)$ K, as a consequence of the decomposition of the low-temperature modification of the $AgGaGeS_4$ compound. The existence of the quaternary compound in two temperature ranges separated by a two-phase region was established. The determined thermodynamic data and thermal stability range of the $AgGaGeS_4$ compound, will facilitate the discovery of new materials with diverse applications.

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Conflict of Interest The authors declare that they have no conflict of interest.

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