INVESTIGATION OF SYNTHESIS AND THERMODYNAMIC PROPERTIES OF SILVER THIOSTANNATES IN WATER AND ETHYLEN GLYCOL CONDITION

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Obtaining condition of silver thiostannates were investigated in water and ethylene glycol conditions based on $AgNO_3$ and SnS_2 compounds by the differential-thermal (DTA), X-ray, scanned electron microscopy (SEM) analysis methods. It has been established that, nano and micro-sized Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ compounds are obtaining when the thermally processing mixture within the mole ratios of $AgNO_3/SnS_2$ = 4:3; 4:5; 2:1; 8:3 and 1:1 at a temperature of (pH = 6÷8) 353-453 K within 48 hours in the water and ethylen glycol conditions. The values of the integral thermodynamic functions of the corresponding compounds of electrical motion force were determined and the standard atomization thermodynamic functions were calculated based on these values. The thermodynamic parameters of the decomposition reactions of $Ag_2Sn_2S_5$, Ag_4SnS_4 and $Ag_4Sn_3S_8$ compounds that were melting incongruently in the temperatures at 955 K, 1043 K and 1147 K were calculated and the equilibrium constants of the corresponding reactions were determined according to the Gibbs free energy value.

Keywords: silver thiostannate, water, ethylene glycol, temperature, electrical motion force, thermodynamic function, micro photo, equilibrium constant, yield

There are Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ compounds in Ag-Sn-S system. These compounds are part of perspectively functional materials and they have semiconductor, photoelectric and thermoelectric properties [1-16]. Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_8SnS_6 və $Ag_4Sn_3S_8$ compounds are used in the electronics industry because they have high semiconductor properties [20].

In recent times, interest has increased about the acquisition of these compounds in the nanoparticles or micro-particles forms. In contrast to monocrystals, better properties are observed in nanoparticles and micro-particles. In this regard, the acquisition of nano and micro particles in the aqueous and organic solvent conditions of Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 və $Ag_4Sn_3S_8$ containing compounds is one of the actual issues [12-20].

There is a few information about the acquiring of silver thiostannates in nanoparticles in aqueous and organic solvent conditions. In this regard, one of the most topical issues is the study of the condition of these compounds as nanoparticles in various organic matter (ethylene glycol, dimethylformamide and ethylenediamine) conditions.

Experimental part and discussion of the results

Silver(I)nitrate and tin(IV)sulfide were used as the starting material for the synthesis of Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ in water and ethylene glycol conditions. Tin(IV)sulfide was obtained by the method known in the aqueous in the impact regularly of tin(II)chloride with H_2O_2 and $CH_3CS(NH_2)$ [12-19].

$AgNO_3/SnS_2$ = 4:3; 4:5; 2:1; 8:3 and 1:1 mixed in mol ratio and the solvent was added according to the stoichiometric structure of Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 və $Ag_4Sn_3S_8$ compounds. The conditions for the reaction have been investigated in aqueous and ethylene glycol environments. The synthesis condition was researched within the range of 353-453 K temperature. Very small amounts of components were used considering the formation of nanoparticles and the presence of tin(IV)sulfide adhesion properties. The required amount of components was mixed and 20 ml of solvent (aqueous and ethylene glycol) was added, three samples were prepared from each compound. The samples were completely mixed then placed in a microwave oven and heated at a temperature of 353-423 K for 48 hours. The precipitated sediments were filtered, initially washing with 0,1 M CH_3COOH solution then washed with ethyl alcohol after all dried in vacuum at 353 K.

The individuality of the obtained compounds and physical-chemical properties were investigated by DTA (Pyrometer HTP-70, Thermoscan-2), X-ray (2D PHASER "Bruker", CuK_α, 2θ, 20-80 deg.) (fig. 1), microstructure analysis methods and EMF measurements.

According to the X-ray results, it was found that the crystallization rate was 57-72% of compounds obtained in aqueous and ethyleneglycol conditions. The Ag_2SnS_3 compound obtained at 453 K is crystallized in the orthorombic syngony: *S.g.: $Pna2_1$; lattice. par.:*

a = 0,6272 nm, b = 0,5795 nm, c = 1,3181 nm; $\beta = 93{,}31^0$ *(Fig. 1).* $Ag_2Sn_2S_5$ compound also is crystallized in the orthorombic syngony: S.g.: $Pna2_1$; lattice. par.: *a = 0,78165 nm, b = 0,7719 nm, c = 1,1121 nm.* Ag_4SnS_4 compound is crystallized in the monocline syngony: S.g.: $Pna2_1$; lattice. par.: *a = 0,69161 nm, b = 0,7112 nm, c = 1,3021 nm;* $\beta = 92{,}5^0$. Ag_8SnS_6 is crystallized in the orthorombic (S.g.: $Pna2_1$; lattice. par.: *a = 1,5334 nm, b = 0,5620 nm, c = 1,07244 nm*), but $Ag_4Sn_3S_8$ compound is cubic syngony (S.g.: $P4_132$; *a = 1,0799 nm; Z = 4*).

An endothermic effect observed at 935 K temperature in the DTA curve of the Ag_2SnS_3 compound, which corresponds to its melting temperature. The compounds $Ag_2Sn_2S_5$, Ag_4SnS_4 and $Ag_4Sn_3S_8$ are respectively incongruent melting at 955 K, 1043 K and 1137 K. It has been determined that these compounds are disintegrate by the following reactions:

$$Ag_2Sn_2S_5 \rightarrow Ag_2SnS_3 + SnS_2 \text{ (955 K)};$$

$$Ag_4SnS_4 \rightarrow Ag_2SnS_3 + Ag_2S \text{ (1043 K)};$$

$$Ag_4Sn_3S_8 \rightarrow 2Ag_2SnS_3 + SnS_2 \text{ (1137 K)}.$$

Polymorphic conversion temperature of Ag_8SnS_6 is 445 K, melting point is 1120 K.

Micromorphology of the samples was studied by HITACHI TM3000 microscope. The analysis of the microscopic images on the bottom of the glass revealed that compounds obtained in aqueous and ethylene glycol conditions are nanoparticles. The particle size is 60-120 nm in the thin layer of the Ag_2SnS_3 compound in the aqueous condition, but in the ethylene glycol condition is 40-100 nm (fig. 2).

The nanoparticles size of the $Ag_2Sn_2S_5$ compound formed at 453K in the ethylene glycol environment are smaller. The nanoparticles size obtain at 423 K are large and the adhesion is more observed among the particles (fig. 4). It was determined that the particles size obtained at 373 K in the aqueous condition is 150-348 nm, and the size of the nanoparticles size taken in the ethylene glycol varies among 318-572 nm. It is known that, the merger with each other of SnS2 molecules and polymerization are occurs when the tin (IV) sulphide is keeped for a certain period of time or processed thermally. This event is observed in many thiostannates of tin, including $Ag_2Sn_2S_5$ compounds.

High adhesive nanorods are obtaining of Ag_8SnS_6 compound at 458 K. The length of the nanorods ranges from 4-10 nm and a diameter of from 82-187 nm. The formation of nanorods in the aquatic environment does not occur. Full formulation is observed in the ethylene glycol condition (fig. 2). The formation of nanorods in the Ag_8SnS_6 compound can be explained by the large amount of silver.

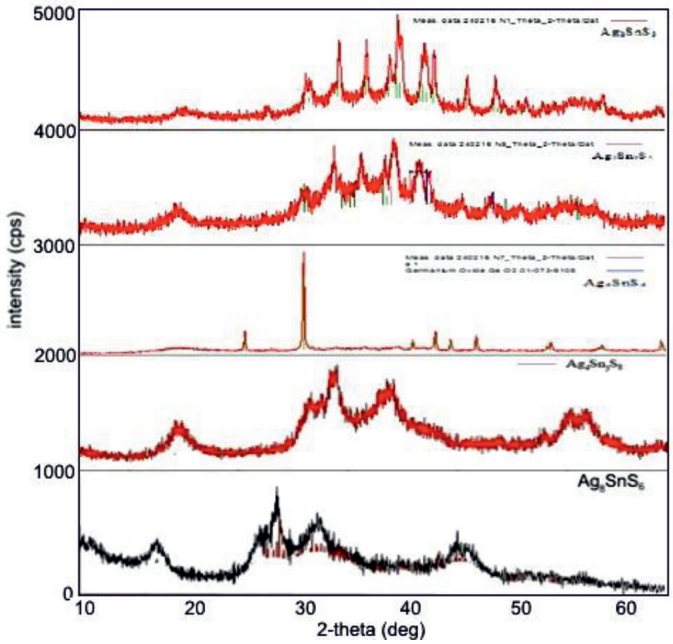

Fig. 1. Diffractograms of the Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ compounds obtained in the ethylene glycol condition

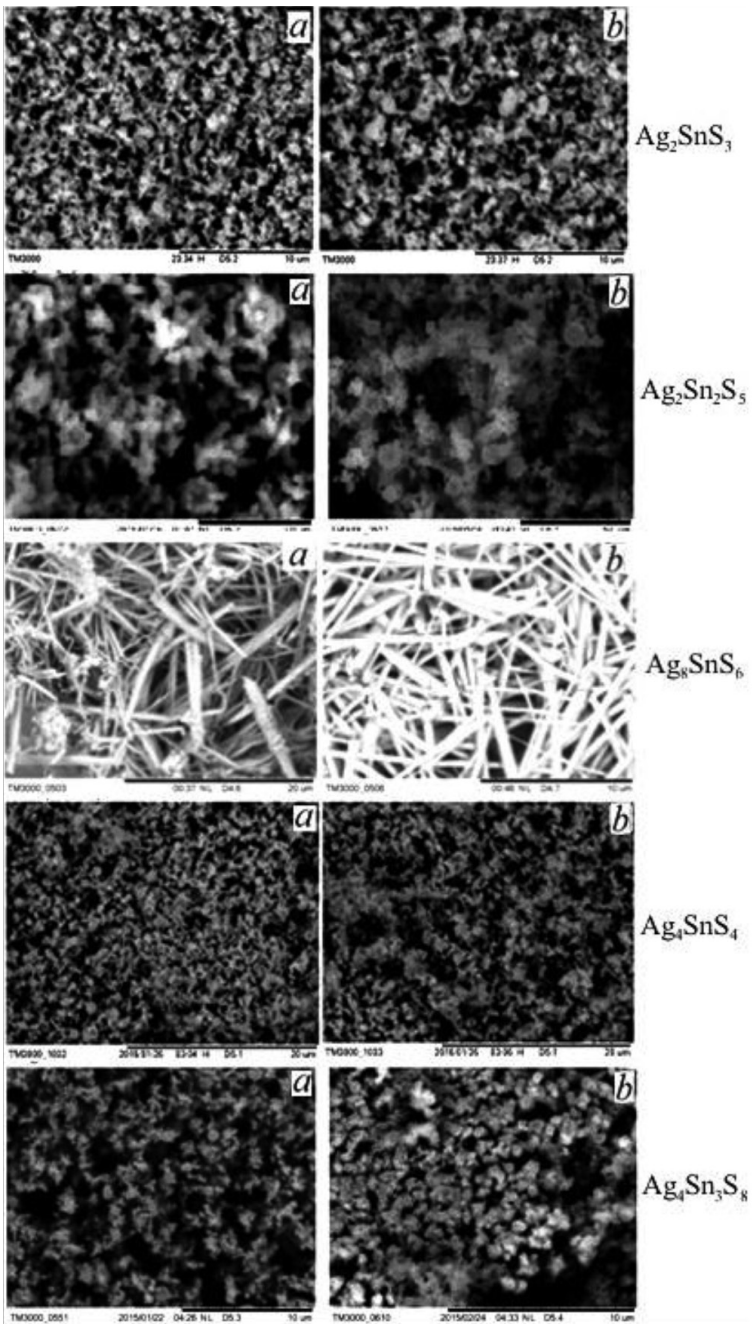

Fig. 2. SEM images of Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, $Ag_4Sn_3S_8$ and Ag_8SnS_6 compounds obtained in water (a-373 K) and ethylene glycol (b-453 K)

The particles of the Ag_4SnS_4 compound in the aqueous condition are 190-230 nm, and the particles obtained in the ethylene glycol condition are 80-140 nm. The particles are zigzagically structured and interconnected (fig. 2). It can be said that the composition of the phase is identical because it does not have a different structure.

Large aggregates are observed in SEM images of $Ag_4Sn_3S_8$ compound. These aggregates size are larger in ethylenglycol (fig. 2). Aggregates are consist of high adhesive particles with a structure size of 98-137 nm. The formation of aggregates in this combination can be explained to the large amount of tin in compound. As can be seen in the SEM images,

no other phase particles in the obtained compound structure of water and ethylene glycol conditions are observed. This also confirms the X-ray results of the $Ag_4Sn_3S_8$ compound. An elemental analysis (Launch Trion XL dilution refrigerator – OXFORD device) of sediment content was made to specify the stoichiometric structure of Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ compounds. According to the results, the mass and atomic proportions of silver, tin and sulphur contained in the compounds were determined (table 1).

According to the results of the table, it has been determined that the stoichiometric structure of the sediments corresponds to Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ compounds. It has been revealed that the composition of sulphur in the simple formulas of compounds is slightly out of (0,07-0,09 at.%) stoichiometry. It can be explained by the fact that, when adding the thioacetamide solution to the initial mixture, some free sulfur is separated because of the condition is acid (pH = 2-2,5). This also shows itself in the composition of synthesized compounds.

Here is also investigated the effects of pH (pH METER-pH410 "AKVILON") and temperature on the yielding of Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ compounds. 0,1 M H_2SO_4 and 0,1 M NH_3H_2O solutions were used to study the impact of pH on condition on the yield of compounds. It has been determined that the compounds have the maximum yield (96,21-97,63%) at the pH range of 6-8 (453 K). The yield is reduced because of the compounds disintegrate at pH < 2 and pH > 9.

The effect of the temperature was studied on the yileding of Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ compounds in pH = 6-8. It was determined that the yileding of Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ compounds increased when temperature increased. Maximum yielding of compounds is observed in temperature range T = 393-453 K. X-ray results show that the crystallization rate of compounds is 57.2 and 65.7%, when the aqueous solution of Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ compounds is thermally processed in autoclave at 453 K for 24 hours.

(-) Ag | Ag_4RbI_5 | Ag_2SnS_3 ($Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 və $Ag_4Sn_3S_8$) (+)

type consentration element has been constructed to make EMF measurements. The results of [1-4, 21-24] studies have been used to prepare the concentration element. EMF measurements were made with a V7-34A brand digital voltmeter and compensation method at a temperature range of 300-430 K. Measurements were accomplished both at the heat and cooling time. At this time, the difference in the measurement results was less than 0.5 mV. EMF–T dependency charts have been established based on the EMF values. Thermodynamic parameters were calculated based on EMF–T dependency. For this purpose, the linear equation was used which is the used in scientific literature [1-3]:

$$E = a + bT \pm t\left[(S_E^2 / n) + S_b^2 \cdot (T - \overline{T})^2\right]^{1/2}$$

Here, the number n – the number of pairs of E and T values; respectively S_E və S_b – dispersion of separated EMF measurements and b coefficients, $\overline{T}$ – average temperature, K; t – the student criterion. The corresponding linear equations have been obtained by the smallest squares method through a special computer program (POWDER-2). The silver parsial thermodynamic functions of Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ compounds were calculated based on the following expressions using the linear equations.

$$\Delta\overline{G}_{Ag} = -zFE\ ;\ \Delta\overline{H}_{Ag} = -zFa\ ;\ \Delta\overline{S}_{Ag} = zFb\ .$$

Integral thermodynamic functions of compounds based on potential generating reactions were calculated using the standard thermodynamic functions values of silver, copper parsial molar functions and corresponding sulfides in literature (table. 2).

The reason for the relatively high rate of error in the prices of integrated integrated temodynamic functions is that Gibbs free energy by EMF is calculated directly and the enthalpy and entropy is calculated from the angular coefficient of temperature dependence of EMF.

Standard atomization thermodynamic functions of corresponding compounds were calculated based on the prices of integral thermodynamic functions of Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ compounds. According to Hess's law, the atomic energy of any complex matter is equal to the subtraction of the formation enthalpy of that compound with the total atomization energies of the appropriate simple substances (Ag, Sn, S) [3]:

$$\Delta H^{at.}_{com.} = \sum \Delta H^{at.}_{elem.} - \Delta H_{com.}$$

The standard atomization thermodynamic functions of Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ compounds were calculated using this expression (table. 3).

Table 1

Results of the elements analysis of compounds

Compounds	Amount of elements, %					
	Ag		Sn		S	
	weight	at.	weight	at.	weight	at.
Ag_2SnS_3	50,11	33,32	27,61	16,66	22,28	50,02
$Ag_2Sn_2S_5$	35,17	22,21	38,76	22,22	26,07	55,57
Ag_4SnS_4	63,62	44,43	17,52	11,11	18,86	44,46
Ag_8SnS_6	73,527	53,32	10,127	6,66	16,346	40,02
$Ag_4Sn_3S_8$	41,13	26,66	34,16	19,98	24,71	71,36

Table 2

Integral thermodynamic functions of Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ compounds

Compounds	$-\Delta_f G^0$	$-\Delta_f H^0$	S^0
	kC/mol		*C/mol·K*
Ag_2SnS_3	213,91 ± 2,3	183,77 ± 7,1	218,03 ± 10,4
$Ag_2Sn_2S_5$	407,45 ± 5,1	351,4 ± 9,3	321,65 ± 9,2
Ag_4SnS_4	234,25 ± 2,5	199,07 ± 4,3	454,8 ± 6,7
Ag_8SnS_6	274,95 ± 1,2	232,67 ± 2,3	609,92 ± 6,8
$Ag_4Sn_3S_8$	724,65 ± 1,3	535,01 ± 2,2	841,3 ± 8,7

Table 3

Standard atomization thermodynamic functions of Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ compounds

Compounds	$-\Delta G^0_{at.}$	$-\Delta H^0_{at.}$	$\Delta S^0_{at.}$
	kC/mol		*C/mol·K*
Ag_2SnS_3	1641,6	1552,8	1354,6
$Ag_2Sn_2S_5$	2840,95	3159,64	1384,75
Ag_4SnS_4	2882,45	3249,02	1413,3
Ag_8SnS_6	4831,7	5477,07	2622,19
$Ag_4Sn_3S_8$	4852,05	5296,21	2034,4

The equilibrium constants of the decomposition reactions of the incongruent melting $Ag_2Sn_2S_5$, Ag_4SnS_4 and $Ag_4Sn_3S_8$ compounds have been determined using the values of the determined thermodynamic parameters. It is known that the products of the decomposition reaction of these compounds are respectively melting at 955 K, 1043 K and 1147 K. When it's cool, the process is returning because the initial substances are obtain. Initially, the conversion of the thermodynamic parameters of decomposition reactions was calculated at the same temperatures:

$Ag_2Sn_2S_5 \rightarrow Ag_2SnS_3 + SnS_2$, $\Delta H = -16,6$ kC; $\Delta G = -20,35$ kC; $\Delta S = 13,22$ C;

$Ag_4SnS_4 \rightarrow Ag_2SnS_3 + Ag_2S$, $\Delta H = -84,74$ kC; $\Delta G = -87,98$ kC; $\Delta S = 92,77$ C;

$Ag_4Sn_3S_8 \rightarrow 2Ag_2SnS_3 + SnS_2$, $\Delta H = -32,6$ kC; $\Delta G = -35,22$ kC; $\Delta S = 33,84$ C.

It is known that when the temperature rises, the value of free energy greatly varies unlike from the enthalpy and entropy. Therefore, equilibrium constants of reactions occurring at melting temperatures were calculated using the following equation [20]:

$$\lg K = -\frac{\Delta G}{19,47 \cdot T}.$$

Table 4

Equilibrium constants of decomposition reactions

Reactions	Temperature, K	lgK	K
$Ag_2Sn_2S_5 \leftrightarrow Ag_2SnS_3 + SnS_2$	955	1,57	37,15
$Ag_4SnS_4 \leftrightarrow Ag_2SnS_3 + Ag_2S$	1043	8,94	$8,7 \cdot 10^8$
$Ag_4Sn_3S_8 \leftrightarrow 2Ag_2SnS_3 + SnS_2$	1147	0,28	1,91

The results obtained are given in the table below (table 4).

As the values of the equilibrium constants shows, the equilibrium reaches right in all three reactions at melting temperatures. Liquid phase is two-component.

Conclusion

Ag_2SnS_3, $Ag_2Sn_2S_5$, Ag_4SnS_4, Ag_8SnS_6 and $Ag_4Sn_3S_8$ compounds were obtained by hydrothermal method and their individuality was confirmed by X-ray, DTA methods in the aqueous and ethylene glycol condition. The micromorphology of the obtained compounds was studied and it was determined that the compounds at 453 K temperature were formed from nanoparticles. The boundaries of obtain of the compounds were determined in hydrothermal conditions. According to EMF measurements, the prices of integral thermodynamic functions of compounds are determined, and the values of the standard atomic thermodynamic functions of compounds based on these values are calculated. The equilibrium constants of the decomposition reactions occurring at melting temperatures of the incongruent melting $Ag_2Sn_2S_5$, Ag_4SnS_4 and $Ag_4Sn_3S_8$ compounds have been determined using Gibbs's free energy value.

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