Investigation of the Acquisition Conditions of Tl_3AsS_4 Compound in the Aquatic Environment

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Abstract: The condition for obtaining the Tl_3AsS_4 compound was investigated based on $TlNO_3$ and As_2S_5 compounds in hydrothermal conditions in the aquatic environment. It was found that Tl_3AsS_4 compound has been obtained from a mixture of the primary components (As_2S_5 and $TlNO_3$) in a ratio of 4:15 mol at 80 °C in the range of pH = 7 – 8. The individuality of the obtained Tl_3AsS_4 compound was confirmed by the XRD method and DTA, and TG analyses. The thermally processed Tl_3AsS_4 compound crystallizes in an orthorhombic structure at 220 °C. Based on the results of TG analysis, the temperatures of the phase transitions that occur during the oxidation of the compound were determined and the stoichiometric composition of the compound was specified. The SEM results of the compound showed that the Tl_3AsS_4 precipitate obtained from the solution at 80 °C is composed of aggregates of highly adherent nanoparticles and the size of the nanoparticles varies from ~60 to 120 nm. The effect of pH of the medium and the amount of the primary components on the yield of Tl_3AsS_4 was studied. It was determined that when T > 100 °C, $(Tl_2S)_x(As_2S_3)_{1-x}$ (x=0.1-0.9) – containing sediments are obtained from different molar ratios of the primary components (As_2S_5 and $TlNO_3$).

Keywords: Functional materials, sediments, chemical analysis, thermogravimetric analysis, micromorphology.

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INTRODUCTION

Thio-compounds created from thallium with arsenic and glass-like alloys obtained based on them are valuable functional materials of semiconductor, photoelectric, acousto-optical properties, etc. The phase equilibrium and glass formation in the Tl-As-S system, as well as the physicochemical properties of the intermediate phases, have been studied in a number of studies (1-7, 13-17, 19, 22). The compounds and alloys in the system are mainly obtained by the direct synthesis method.

The Tl-As-S system was first studied by Prerichs, and glass formation was observed in the polythermal incision of As_2S_3 – Tl_2S_3 in the area of 15 and 50% (w) Tl_2S_3 concentration (19). The synthesis was performed in H_2S flux in open quartz ampoules.

Glass formation on the incision of As_2S_3 – Tl_2S was studied by Goryunov, Kolomiych and Shilov (5, 6, 12). The glass formation was carried out by vacuum synthesis method at a temperature of 900 °C, cooling was carried out at a slow speed (1 deg/sec). Glass formation was observed in areas of 50-70 mol % Tl_2S concentration.

The boundaries of glass formation and properties in the Tl-As-S system were studied by Flashchen (3,4).

The glasses were obtained by the method of direct synthesis in quartz ampoules based on elemental (Tl, As, S) components. The cooling process was conducted slowly. In the system, stratification was observed in sulfur-rich areas. The melting temperature of the glass was determined by the dilatometric method. It was found that the melting point decreases as the amount of Tl in the glass increases.

The boundaries of glass formation in the Tl-As-S system have been repeatedly studied by Markova (16). The glasses were obtained by vacuum synthesis method based on elemental components at 850 °C for 1 – 2 hours. Hardening is completed in 10 – 12 hours with slow cooling. Alloys riched with Tl were hardened in air or water. It was found that stratification was observed in alloys under such conditions. During slow cooling, glasses are obtained up to 15% Tl concentration areas. The results of the (16) study are slightly different from the results of Flashchen (3,4). The glass obtained from the Tl-As-S system is resistant to weather conditions. It was found that when the amount of Tl_2S in glass increases from 7.2 to 50 mol%, the melting temperature decreases from 147 to 96 °C, respectively (13, 14).

The phase equilibrium in the As_2S_3-Tl_2S system was investigated and 4 chemical compounds (Tl_3AsS_3, $Tl_4As_2S_5$, $Tl_6As_4S_9$ and $TlAsS_2$) were found (2). The phase diagram of this system was created by the authors (13, 14). A long-term (400 hours) thermal process was performed to crystallize glass-like alloys. The $TlAsS_2$ triple compound observed in the system melts congruent at 280 °C while the Tl_3AsS_3 and $TlAs_3S_5$ compounds melt incongruent at 290 and 220 °C, respectively. It was found that the As_2S_3-$TlAsS_2$ system has formed a eutectic-type phase diagram. Eutectic is in the area of ~70 mol% As_2S_3 concentration and melts at 190 °C. Stratification is observed in the $TlAsS_2$-Tl_2S system and the monotectic temperature is 300 °C. Between $TlAsS_2$ and Tl_3AsS_3 compounds, eutectic is formed in the 35 mol% compositions of As_2S_3 and the melting point is 220 °C. Solid solutions based on Tl_2S were obtained in the As_2S_3-Tl_2S system (13, 14). $TlAsS_2$ is found in nature as a lorandite mineral and crystallizes in monoclinic syngony (21).

Recent literature shows that Tl_3AsS_4, $TlAsS_2$, Tl_3AsS_3, $TlAs_3S_5$, $Tl_3As_5S_{10}$, $Tl_9As_5S_{15}$, $Tl_9As_3S_{13}$, Tl_3AsS_6 and $Tl_8As_2S_9$ compounds are available in the Tl-As-S system (1, 17).

The interaction between Tl_2S-As_2S_3 with the co-precipitation method from aqueous solutions was studied by the microscopic method in 1907 (9). Homogeneous precipitates were obtained based on Tl^+ and As^{3+} salts in acidic and alkaline solutions by co-precipitation with H_2S. It was found that only sediment which is composed of 62 mol% As_2S_3 is a two-phase. According to the authors, solid solutions are obtained up to 62 mol% As_2S_3 concentration area in the As_2S_3-Tl_2S system. Tl_3AsS_4 compounds were obtained by the co-deposition method using aqueous solutions of Tl^+ and As^{5+} salts and alkali metal sulfides as sulfidation reagents (2). It was found that the compound Tl_3AsS_4 melts incongruently, its decomposition temperature is 250 °C.

In modern times, the production of a number of binary and triple sulfides from aqueous solutions is one of the most pressing issues, because the compounds obtained in aqueous solutions are in the form of nano- and microparticles. By controlling the size and shape of particles of known materials, it is possible to change their properties and identify new areas of application. In this regard, the acquire of very small-sized and new featured materials is of great interest. The literature provides information on the study of micromorphology of $AgAsS_2$, Ag_3AsS_3, $CuAsS_2$ and Cu_3AsS_3 compounds obtained by hydrochemical and hydrothermal methods (7,8).

The aim was to study the interaction between $TlNO_3$ and As_2S_5 in the aquatic environment and to obtain the Tl_3AsS_4 compound individually. The article presents the results of the study of the conditions for the acquisition of Tl_3AsS_4 in the aquatic environment and some physical-chemical properties.

EXPERIMENTAL SECTION

Chemicals

Arsenic(V) sulfide for this research was initially obtained using chemicals sodium arsenate, hydrochloric acid, hydrogen sulfide gas. Furthermore, arsenic(V) sulfide which is obtained in high purity and thallium nitrate were used to obtain the thallium tetrathioarsenate compound. All chemicals used in experimental studies were provided as high purity products, and whole reactions were conducted in ultra-clean water. Besides, distilled water and ethanol were used to wash the obtained precipitate. Moreover, ammonium molybdate and hydrazine solutions were used to analyze arsenic in sediment samples and leachate. All of the chemicals used during this study are of analytical grade.

Instrumental techniques

The following instruments were used for measurement and characterization: X-ray Diffraction (XRD) analysis of samples was performed by a Bruker D2 Phaser XRD. Thermogravimetric (TG) and differential thermal analysis (DTA) data were recorded using the NETZSCH STA 449F3 instrument. Scanning Electron Microscopy (SEM) image for the investigation of the surface morphology is taken by the HITACHI TM3000 microscope. Glassco 710.AG.01 magnetic heater&stirrer (350 °C/1600 RPM) have been used for heating and stirring reaction solution. The pH measurements were carried out with an "аквилон" pH – 410 at room temperature. "КФК – 2 – УХЛ 4.2" photo calorimeter was used to determine the arsenic content of the initial reaction filtrate and the precipitate obtained. KD (WBFY-201) professional chemical microwave oven has been used for the formation of sediment.

Synthesis of Tl_3AsS_4 Compound

According to the known methodology, as an initial component to obtain the Tl_3AsS_4 compound, the As_2S_5 compound was obtained by mixing a 0.5 g Na_3AsO_4 compound acidified with 10 N hydrochloric acids and releasing H_2S gas in a temperature range of 0 – 10 °C for 2 hours (11). The system was cooled with ice water. In this case, the following reaction occurs:

$$2Na_3AsO_4 + 5H_2S + 6HCl \rightarrow As_2S_5 + 6NaCl + 8H_2O \quad (1)$$

0.35 g of As_2S_5 and 1.12 g of $TlNO_3$ were mixed to obtain the Tl_3AsS_4 compound in the aquatic environment. The reaction mixture was stirred in a magnetic stirrer for 3 hours, then the precipitate was filtered, after which it first washed with distilled water and then with ethanol. The sediment kept in a microwave oven under hydrothermal conditions (80 °C) for 78 hours by adding ultra-clean water again. The pH of the condition was kept in the range of 7 - 8. The equation of the reaction can be summarized as follows:

$$4As_2S_5 + 15TlNO_3 + 12H_2O \rightarrow 5Tl_3AsS_4 + 3H_3AsO_4 + 15HNO_3 \quad (2)$$

After thermal processing, the sediment was filtered, washed, and dried at 100 °C under vacuum (~10^{-1} Pa).

RESULTS AND DISCUSSION

Chemical Analysis

Obtaining the Tl_3AsS_4 compound was carried out based on the results of a number of experimental studies. The sample taken from the precipitate of the Tl_3AsS_4 compound was dissolved in concentrated HNO_3 and completely evaporated. Upon completion of the complete evaporation process, the volume of the dry residue was clarified to 100 mL. A sample was taken from the diluted solution and then ammonium molybdate and hydrazine solution were added to it. This solution was heated in a water bath for 10 minutes. In this case, arsenomolybdate blue has been formed. The amount of arsenic in the sediment was determined by the colorimetric method in a sample taken from the blue solution (18). Besides, the amount of arsenic in the filtrate after the initial reaction was determined by the same method. The table below shows the results of 8 experiments (Table 1.). Chemical analysis methods determined (20) that the amount of precipitate obtained and the amount of As^{+5} ion transferred to the solution during the interaction of the initial components taken in the amount corresponding to the stoichiometric composition of Tl_3AsS_4 between pH = 7 and 8 corresponds well to the reaction (2).

Table 1. The amount of obtained Tl_3AsS_4 sediment and passed components to the solution during the reactions.

Experiment	As_2S_5, g	$TlNO_3$, g	Tl_3AsS_4 sediment, g	The amount of As^{+5} ion transferred to the solution, g
1	0.3500	1.1278	1.0251	0.0631
2	0.4011	1.2925	1.3199	0.0704
3	0.5002	1.6118	1.6325	0.0896
4	0.4922	1.5860	1.6095	0.0883
5	0.3944	1.2709	1.2703	0.0604
6	0.3539	1.1404	1.1315	0.0589
7	0.3098	0.9983	0.9968	0.0476
8	0.3321	1.0701	1.0658	0.0518

XRD Analysis

The obtained Tl_3AsS_4 sediment was thermally processed at a temperature of 220 °C in a vacuum (~ 10^{-2} Pa) for 2 hours and its composition was checked by XRD. It was found that the sediment consists of the Tl_3AsS_4 compound and has an orthorhombic structure (Space gr.: Pnma; lattice. par.: $a = 0.9268$ nm, $b = 0.9334$ nm, $c = 1.1123$ nm, $\alpha = \beta = \gamma = 90^0$). The values of the intensity peaks in the diffractogram were well matched with the results of other studies (1, 17, 22) (Fig. 1).

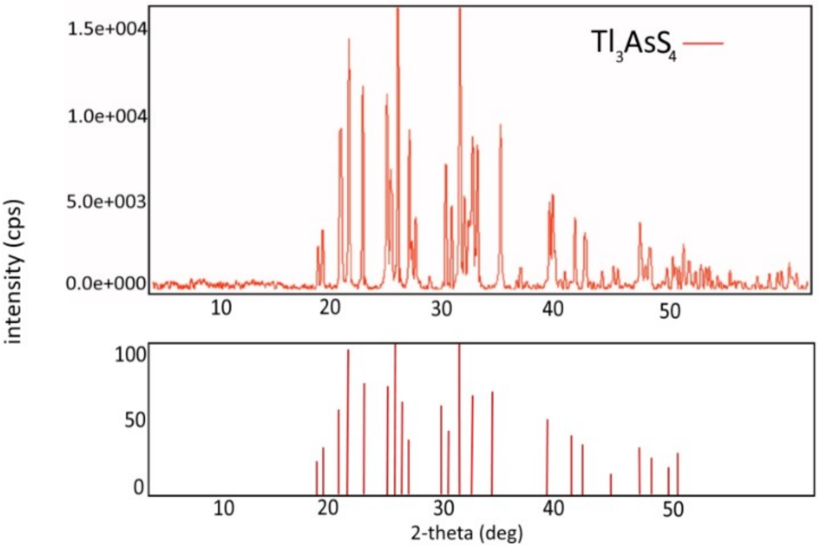


Figure 1. Diffractogram of the Tl_3AsS_4 compound.

TG Analysis

A thermogravimetric (TG) analysis was performed to determine the stoichiometric composition of the obtained Tl_3AsS_4 compound (Fig. 2). The heating process was carried out in a flow of oxygen. As can be seen from the thermogravimetric curve of the compound, the decomposition of the compound begins at 180 °C. Melting of the sulfur separated from the sample occurs in the temperature range of 260-300 °C. The As_2S_3 compound formed in the temperature range of 310-360 °C melts. The exact decomposition of the Tl_3AsS_4 compound is completed at 680 °C, and the maximum mass loss in a 36 mg of sample is 3.61 mg. This is well compatible with the stoichiometric composition of the Tl_3AsS_4 compound. Oxidation of decomposition products occurs when was T > 680 °C and exact oxidation ends at 810 °C. 1.91 mg of oxygen combined with 32.39 mg of the decomposition product. Complete decomposition of oxidation products was observed at 900 °C. After TG analysis, the X-ray results of the remaining residues showed that the sample residue obtained in the temperature range 180-300 °C contains Tl_3AsS_3 + S compounds, in the range of 300-680 °C contains Tl_3AsO_3 compound, in the range of 690-810 °C contains Tl_3AsO_4 compound, finally, in the range of 810-900 °C contains Tl_3AsO_3 compound. The reaction equations based on the X-ray results can be written as follows:

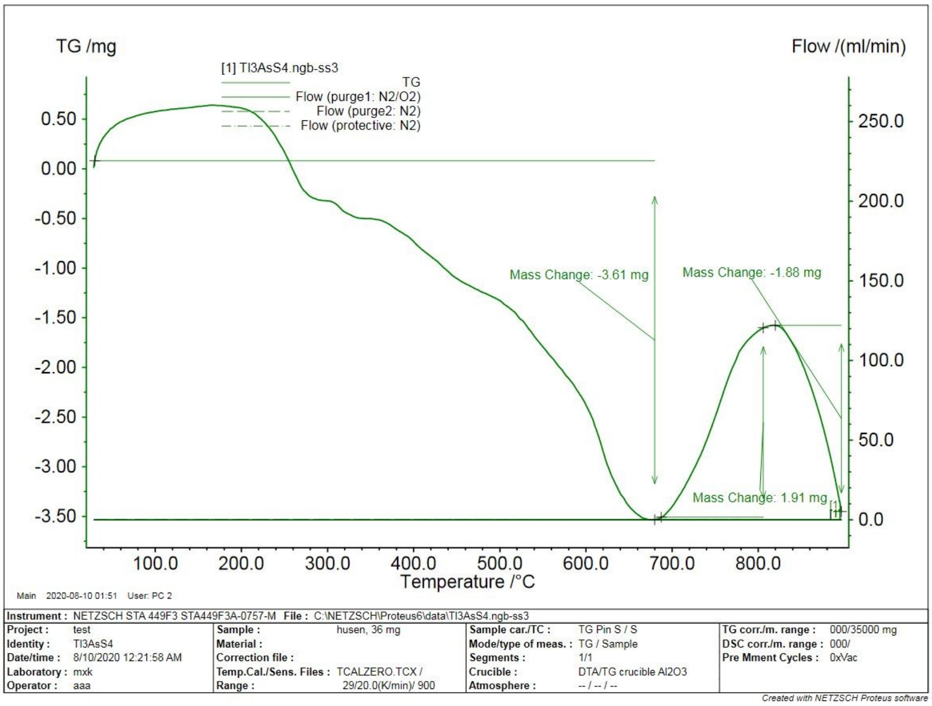
$Tl_3AsS_4 \rightarrow Tl_3AsS_3 + S$ (180-300 °C);
$2Tl_3AsS_3 + 9O_2 \rightarrow 2Tl_3AsO_3 + 6SO_2$ (300-680 °C);
$2Tl_3AsO_3 + O_2 \rightarrow 2Tl_3AsO_4$ (690-810 °C);
$2Tl_3AsO_4 \rightarrow 2Tl_3AsO_3 + O_2$ (810-900 °C).

DT Analysis

DT analysis of Tl_3AsS_4 was conducted in an inert (N_2 gas flow) environment. Thermal effects were observed in the DTA curve of Tl_3AsS_4 at 265 °C and 419.8 °C (Fig. 3). The weak thermal effect observed at 265 °C can be considered as the attenuation or polymorphic conversion temperature of Tl_3AsS_4. The thermal effect at 419.8 °C corresponds to its melting point. The reason for the relatively low melting point can be explained by the fact that the compound is in nanoparticle form. It is known that the melting point of nanoparticles of the same substance is lower than the melting point of its monocrystals (10).

SEM Imaging

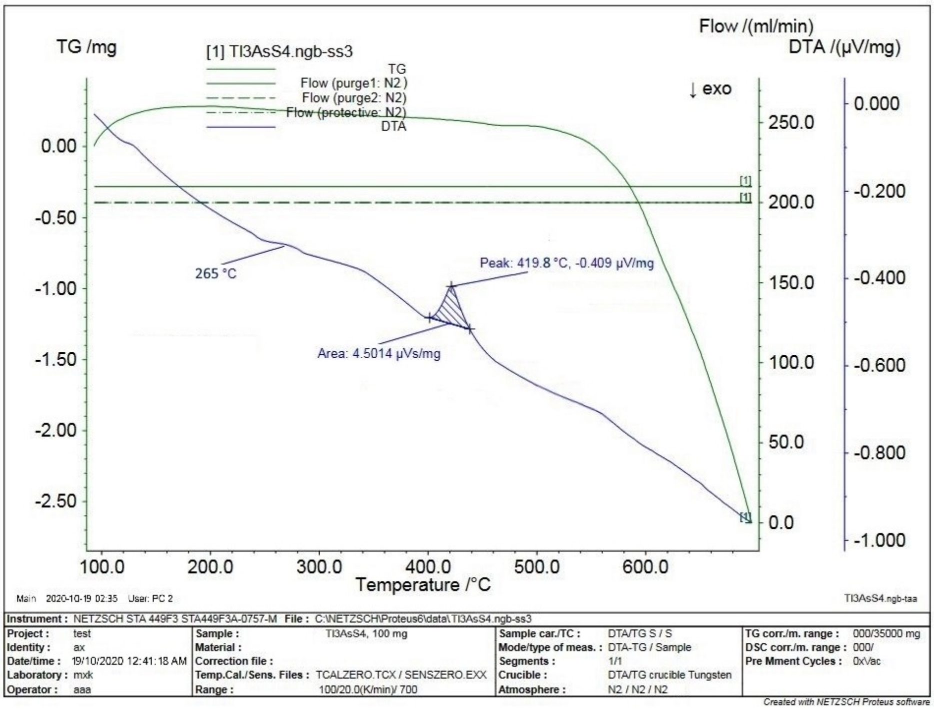
The micromorphology of the Tl_3AsS_4 compound obtained at 80 °C was studied. The size and shape effects of particles in an area of 10 micrometers were determined. As can be seen from the SEM image of the compound, the sediment from the solution is composed of aggregates of highly adhesive nanoparticles (Fig. 4). The size of nanoparticles varies in the range of ~ 60 - 120 nm. It has been found that the particle size increases as the crystallization degree increases when the temperature increases (T > 80 °C).



Instrument : NETZSCH STA 449F3 STA449F3A-0757-M File : C:\NETZSCH\Proteus6\data\Tl3AsS4.ngb-ss3

Project :	test	Sample :	husen, 36 mg	Sample car./TC :	TG Pin S / S	TG corr./m. range :	000/35000 mg
Identity :	Tl3AsS4	Material :		Mode/type of meas. :	TG / Sample	DSC corr./m. range :	000/
Date/time :	8/10/2020 12:21:58 AM	Correction file :		Segments :	1/1	Pre Mment Cycles :	0xVac
Laboratory :	mxk	Temp.Cal./Sens. Files :	TCALZERO.TCX /	Crucible :	DTA/TG crucible Al2O3		
Operator :	aaa	Range :	29/20.0(K/min)/ 900	Atmosphere :	-- / -- / --		

Figure 2. Thermogram of the compound Tl_3AsS_4.



Instrument : NETZSCH STA 449F3 STA449F3A-0757-M File : C:\NETZSCH\Proteus6\data\Tl3AsS4.ngb-ss3

Project :	test	Sample :	Tl3AsS4, 100 mg	Sample car./TC :	DTA/TG S / S	TG corr./m. range :	000/35000 mg
Identity :	ax	Material :		Mode/type of meas. :	DTA-TG / Sample	DSC corr./m. range :	000/
Date/time :	19/10/2020 12:41:18 AM	Correction file :		Segments :	1/1	Pre Mment Cycles :	0xVac
Laboratory :	mxk	Temp.Cal./Sens. Files :	TCALZERO.TCX / SENSZERO.EXX	Crucible :	DTA/TG crucible Tungsten		
Operator :	aaa	Range :	100/20.0(K/min)/ 700	Atmosphere :	N2 / N2 / N2		

Figure 3. DTA curve of Tl_3AsS_4 compound.

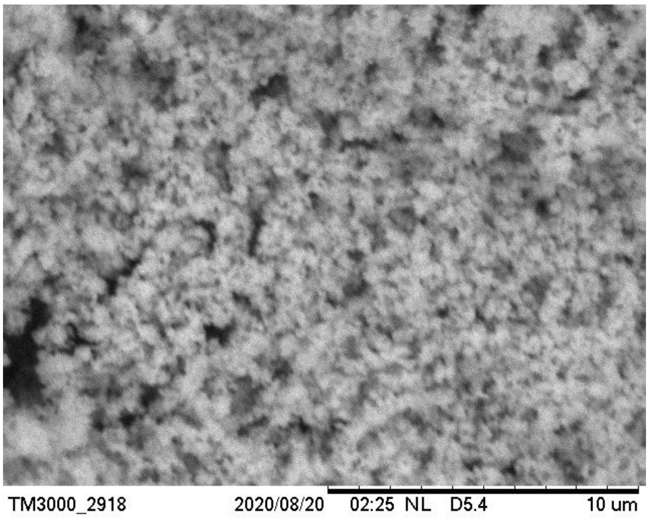


Figure 4. SEM image of the Tl_3AsS_4 compound.

Effect of the pH of the solution

Physical-chemical analysis methods (XRD, DTA) have shown that the yield of Tl_3AsS_4 depends on the pH of the condition. Thus, there is no reaction between the primary components ($TlNO_3$ and As_2S_5) between pH = 1 and 4. The reaction occurs weakly between pH = 4 and 7 and becomes fast between pH = 7 and 8. A mixture of thio- and oxysalts are obtained when was pH > 8.

It was found that when was pH = 7 – 8, depending on the amount of the primary components (As_2S_5 and $TlNO_3$), $(Tl_2S)_x(As_2S_3)_{1-x}$ (x=0.1-0.9) – containing sediments were obtained in the solution. It is known that when the temperature is T > 90 °C, As_2S_5 decomposes by the reaction $As_2S_5 \rightarrow As_2S_3 + 2S$. When the temperature is T < 90 °C, Tl_3AsS_4 is obtained from the amount taken in the appropriate ratio (4:15 mol) corresponding to reaction (2).

CONCLUSION

Tl_3AsS_4 was obtained by hydrothermal method (T = 80 °C and pH = 7 – 8) based on $TlNO_3$ and As_2S_5 compounds and formation conditions have been studied. It was found that the reaction between As_2S_5 and $TlNO_3$ at 80 °C was completed within 3 hours. As_2S_5 decomposes when the synthesis temperature was T > 100 °C and therefore a mixture of thioarsenites ($TlAsS_2$, Tl_3AsS_3) was obtained. The individuality of the obtained Tl_3AsS_4 compound was confirmed by the XRD method. It was found that the thermally processed Tl_3AsS_4 compound crystallized in the orthorhombic structure at 220 °C. It was determined by the TG analysis method that the exact decomposition of the Tl_3AsS_4 compound was completed at 680 °C. The stoichiometric composition of the compound was determined based on the decomposition and oxidation products. The SEM results showed that the Tl_3AsS_4 sediment obtained from the solution was composed of aggregates of highly adhesive nanoparticles. The complete formation of the particles was completed in 78 hours at a temperature of 80 °C. The effect of pH of the medium and the amount of the primary components on the yield of Tl_3AsS_4 were studied. Between pH 7 and 8, Tl_3AsS_4 compound was obtained from a mixture taken at a ratio of 4:15 mol, depending on the amount of the primary components (As_2S_5 and $TlNO_3$). When T > 100 °C, $(Tl_2S)_x(As_2S_3)_{1-x}$ (x=0.1-0.9) – containing sediments were obtained from mixtures of different mole ratios.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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