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STUDY OF THE CONDITIONS FOR THE ACQUISITION OF Tl_3AsS_4 IN ETHYLENE GLYCOL

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Abstract: *The article presents the results of obtaining thallium thioarsenate in ethylene glycol medium and physicochemical analysis methods (XRD, DTG, TG and SEM). It was found that when ethylene glycol is used as a solvent and $TlNO_3$ and As_2S_5 as the initial component, thallium thioarsenate is obtained at 353 K temperature. Thallium thioarsenate is formed by the interaction of $TlNO_3$ and As_2S_5 at a ratio of 4:15 mol. After the compound was obtained at a temperature of 353 K (pH = 7-8), thermally processed at a temperature of 523-543 K, the melting point of the thallium thioarsenate sample has been 683 K. According to the results of thermogravimetric analysis, at temperatures above 733 K thallium thioarsenate decomposes in nitrogen gas environment. The micromorphology of the Tl_3AsS_4 compound obtained in the ethylene glycol medium was studied and it was determined that nanoparticles of the Tl_3AsS_4 compound are formed at a temperature of 353 K.*

Keywords: *thermogravimetric analysis, ethylene glycol, melting point, micromorphology, thallium thioarsenate, nanoparticles*
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Introduction

The compounds formed by thallium with arsenic and glass-like alloys obtained on their basis are valuable functional materials with semiconducting, photoelectric, acousto-optical etc. properties.

The chemical compound, Tl_3AsS_4, has first been obtained as a precipitate by Hawley through adding sodium polysulfide to an aqueous solution containing five-valent arsenic salts. However, the compound obtained by this method had a very small degree of crystallization. It is known that the optical and optoacoustic properties of Tl_3AsS_4 have not been studied in detail before [1]. Orange-red orthorhombic crystals of Tl_3AsS_4 were synthesized by the hydrothermal method. In some Tl-sulfides, as well as in natural and synthetic Tl – thiosalts, Tl-Tl and Tl-S distances and coordination numbers (cn) have been determined [2]. In addition, another study has provided information on obtaining, physical-chemical analysis and microstructures of Tl_3AsS_4 nanoparticles under hydrothermal conditions [3].

As is known, crystals of triple chalcogenides, as well as TI_3AsS_4, are used as elements of acousto-optical filters operating in the infrared region of the spectrum [4]. Despite the unique acousto-optical properties in the infrared range of the spectrum, single crystals of ternary thallium chalcogenides Tl_3AsSe_3, Tl_3AsS_4, Tl_3PSe_4, Tl_3VS_4, $TlGaSe_2$, $TlGaS_2$, $TlInSe_2$, Tl_3TaS_4 and Tl_3TaS_4 have not been sufficiently studied. The Tl_3AsS_4 combination has high optical transmission, low acoustic losses at high frequencies, and good chemical and mechanical properties. For this reason, the authors pointed out that it can be used in acousto-optical devices [4-7].

Phase equilibrium and glass formation in the Tl-As-S system, as well as the physical and chemical properties of the intermediate phases have been studied in several studies [8-9,10]. The compounds and alloys in the system are mainly obtained through direct synthesis.

It is clear from the above literature that very little is known about the acquisition and study of the properties of Tl_3AsS_4 in the solutions of organic compounds. Taking this into consideration, we aimed to investigate the interaction between $TlNO_3$ and As_2S_5 in an ethylene glycol medium and obtain the Tl_3AsS_4 compound individually.

Experimental part

With allowance for methods first mentioned in the literature [11], by the following reaction the As_2S_5 sample was obtained by releasing H_2S gas in 2 hours from a solution of 0.5 g of sodium arsenate containing 0.18 g of arsenic in ethylene glycol, acidified with 10 N hydrochloric acids.

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

To obtain the thallium thioarsenate compound, 0.33 g of As_2S_5 and 1.06 g of $TlNO_3$ (As_2S_5 / $TlNO_3$ = 4 : 15 mol ratio) were mixed by adding 50 ml of ethylene glycol. Using 0.1 M ammonium hydroxide, the pH of the medium was kept in the range of 7-8 and the reaction mixture was mixed (Glassco 710.AG.01 magnetic heater&stirrer (350 °C/1600 RPM) with a magnetic stirrer for 3 hours, at the end of the process the precipitate was filtered, first washed with distilled water and then with ethanol. Chemically pure ethylene glycol was added to the sediment and stored in a microwave oven (KD WBFY-201) at 353 K for 78 hours. The equation of the reaction can be summarized as follows:

$$4As_2S_5+15TlNO_3+12C_2H_6O_2\rightarrow 5Tl_3AsS_4+3H_3AsO_4+15HCl+12C_2H_4O \quad (2)$$

At the end of the process, the precipitate was re-filtered, washed and dried in a vacuum ($\sim 10^{-1}$ Pa) at a temperature of 363 K.

Results and discussion

Chemical analysis. The study of the conditions for the production of Tl_3AsS_4 was carried out based on the results of a number of experimental experiments. A sample of a certain amount of Tl_3AsS_4 was dissolved in nitric acid and the solution was completely evaporated. The dry residue was dissolved in distilled water and made up to 100 ml. The amount of arsenic in the solution was determined by colorimetric method (KFK - 2 - UHL 4.2) [14]. For this purpose, several samples were taken from the solution, ammonium molybdate and hydrazine solution was added to them and boiled in a water bath for 10 minutes. In this case, the optical densities of arsenomolybdate blue complexes formed in solutions were measured and the amount of arsenic was determined in the degree curve. In addition, the amount of arsenic in the filtrate was determined by the same method. The amount of thallium was determined in a separate sample according to the known methodology [12]. The results of chemical analysis, the mass of the sediment, the amount of As^{+5} ions passed to the solution show that the composition of the sample corresponds to the formula Tl_3AsS_4. The results of the determination of the mass of the compound obtained and the amount of As^{+5} ions passed to the solution are given in Table 1.

It was found that when was pH=7–8 and T>373 K, $(Tl_2S)_x(As_2S_3)_{1-x}$ (x = 0.1 – 0.9) – containing sediments were obtained from mixtures of primary components (As_2S_5 and $TlNO_3$) in other mole ratios in the solution. It is known that when the temperature is T > 363 K, As_2S_5 decomposes by the reaction $As_2S_5 \rightarrow As_2S_3 + 2S$. When the temperature is T < 363 K, Tl_3AsS_4 is obtained from the amount taken in the appropriate ratio (4 : 15 mol) corresponding to reaction (2).

Table 1. Determination of the mass of thallium thioarsenate obtained and the amount of As^{+5} ions passed to the solution.

As_2S_5, g	$TlNO_3$, g	Tl_3AsS_4 sediment, g		The amount of As^{+5} ion transferred to the solution, g	
		Experimental	Theoretical	Experimental	Theoretical
0.3300	1.0634	1.0318	1.0862	0.0507	0.0598
0.4397	1.4169	1.3864	1.4473	0.0689	0.0797
0.4928	1.5880	1.5230	1.6221	0.0786	0.0894
0.3862	1.2445	1.1369	1.2712	0.0592	0.0700
0.3643	1.1739	1.1038	1.1991	0.0541	0.0661
0.5705	1.8384	1.7257	1.8778	0.0907	0.1035
0.3027	0.9754	0.8869	0.9963	0.0413	0.0549
0.4631	1.4923	1.5096	1.5243	0.0762	0.0840

The results of chemical analysis of the composition of the compound (thallium, arsenic and sulfur) are given in Table 2.

Table 2. Chemical analysis of Tl_3AsS_4

Amount of sample	Amount of elements,%					
	Tl		As		S	
	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental
0.815	0.612	0.602	0.075	0.071	0.128	0.123

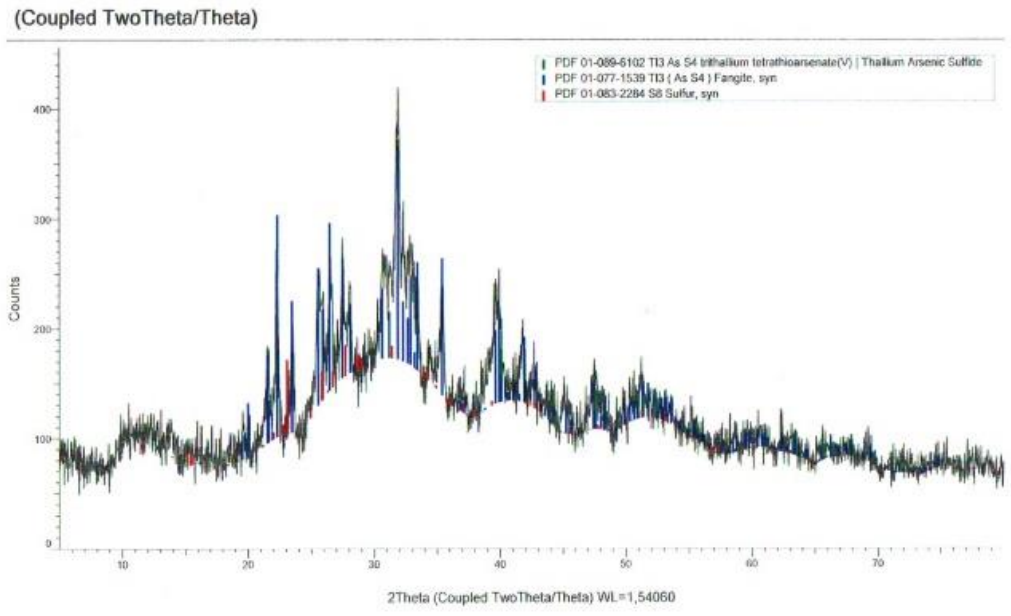


Figure 1. Diffractogram of thallium thioarsenate in ethylene glycol medium at 353 K

Based on the results of chemical analysis of the sample, it was determined that the composition of the compound corresponds to thallium thioarsenate.

XRD Analysis. X-ray phase analysis (D2 PHASER "Bruker", CuKα, 2θ, 20-80 degrees) of the sediment obtained in an ethylene glycol medium at 353 K temperature showed that the main ingredient is tallium tioarsenate (Tl_3AsS_4). It contains a small amount (0.02%) of a mixture of free sulfur (S_8). This is clearly indicated by the intensity maxima in the diffractogram (Figure 1).

The thallium thioarsenate sample was thermally processed at 523-543 K (~10^{-2} Pa vacuum) for 2 hours and its composition was checked by X-ray analysis (2D PHASER "Brooker", CuKα, 2θ, 20-80 degrees). 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 = 0.9339 nm, c = 1.1128 nm, $\alpha = \beta = \gamma = 90^0$). The results of the sample analysis are consistent with the PDF (01-077-1539) value and confirm its individuality (Figure 2).

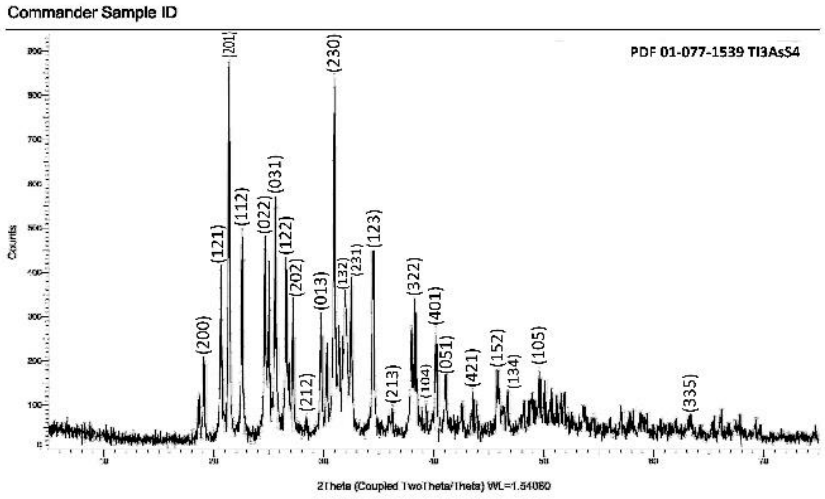


Figure 2. Diffractogram of thermally processed Tl_3AsS_4 compound at 543

SEM imaging. The micromorphology of the Tl_3AsS_4 compound obtained in an ethylene glycol medium at 353 K temperature was studied under a HITACHI TM3000 microscope. As can be seen from the SEM figure in the 5 and 10 micrometer area of the compound, the sediment from the solution is composed of aggregates of nanoparticles (Fig. 3). It is clear from the SEM images that it was not possible to determine the size of the thallium thioarsenate nanoparticles because they were shapeless.

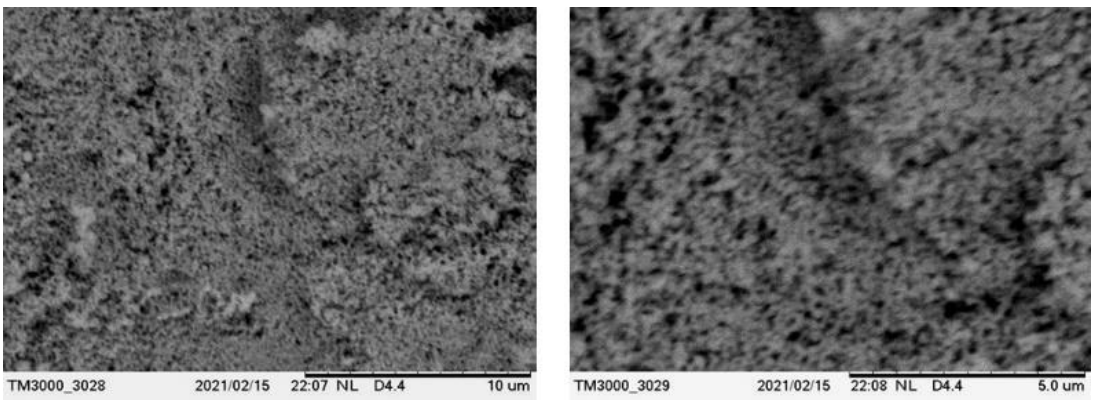
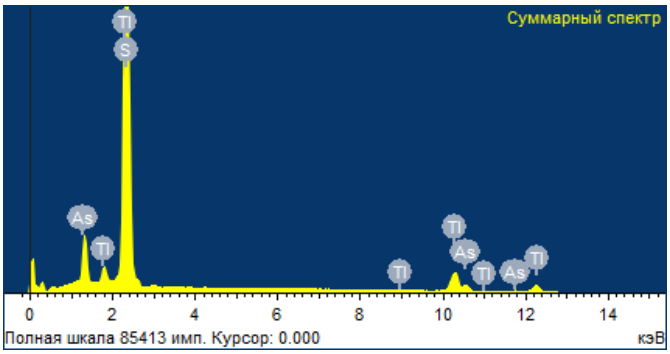


Fig. 3. SEM image of the Tl_3AsS_4 compound.

Elemental analysis. In order to determine the stoichiometric composition of the Tl_3AsS_4 compound, elemental analysis of the composition of the obtained compound was carried out; energy-dispersion spectrum and electronic images were taken (Fig. 4,5), (Launch Trion XL dilution refrigerator – OXFORD device)). Based on the results, the mass and atomic ratios of thallium, arsenic and sulfur in the compounds were determined. Proceeding from the results of elemental analysis, it was established that the simple formula of the compound obtained in ethylene glycol medium is Tl_3AsS_4.



Element	Mass,%	Atom%
S	14.89	48.50
As	9.05	12.62
Tl	76.07	38.88
Cəm	100.00	

Fig. 4. Element composition and energy-dispersion spectrum of Tl_3AsS_4 compound

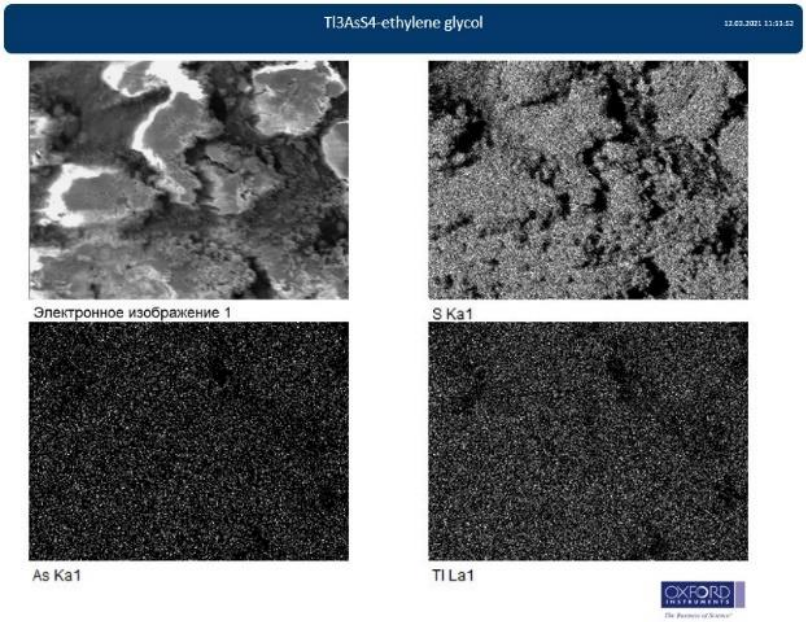


Fig. 5. Electronic images of Tl_3AsS_4

TG/DTG/DTA analysis. TG, DTA and DTG analysis (NETZSCH STA 449F3) of thallium thioarsenate obtained in ethylene glycol medium at 353 K was performed (Figure 6). As can be seen from the thermogram, at a temperature of 573 K, adsorbed substances (gases, ethylene glycol) are released in the Tl_3AsS_4 compound. At this temperature, the total mass loss is 0.28%. Melting of thallium thioarsenate occurs at relatively low temperatures (~ 683 K). Due to the sulfur content of the sediment, this can be clearly seen from the deep endothermic effects on the DTA curve. At a temperature of 733–773 K, sulfur is released from the compound. In this case, the mass loss is 11.24%. Arsenic sublimates as a result of the decomposition of thallium thioarsenate in the temperature range 733–938 K. In this case, the mass loss is 26.19%, which corresponds to the total mass of arsenic and

sulfur in the compound. At a temperature of 948–983 K, thallium azide is formed, after which the sample decomposes as the temperature rises. The results of chemical and X-ray analysis showed that the main component of the residue is free thallium metal.

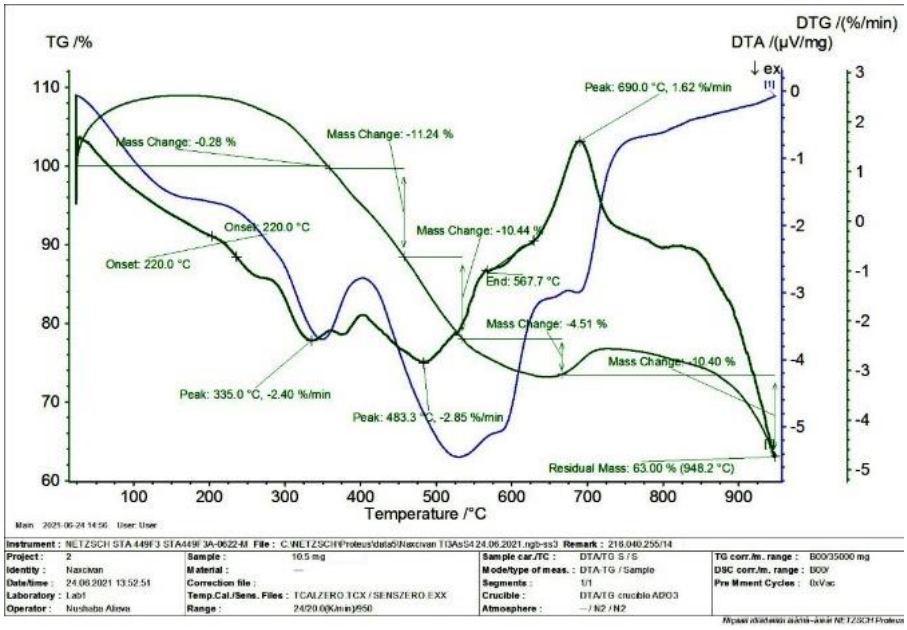


Figure 6. TG, DTG, DTA curves of thallium thiorsenate compound

Conclusion

Tl_3AsS_4 compound was obtained at 353 K temperature on the basis of As_2S_5 and $TlNO_3$ components in ethylene glycol medium. It was determined that this compound was obtained at a ratio of 4:15 moles of the initial components and a pH range of 7–8. The individuality of the Tl_3AsS_4 sample obtained in ethylene glycol medium and at a temperature of 353 K was confirmed by X-ray analysis after heat treatment at a temperature of 523 - 543 K. The elemental composition of the compound was specified and the energy-dispersion spectrum was plotted. The micromorphology of the Tl_3AsS_4 compound was studied and it was not possible to determine the size of the thallium thioarsenate nanoparticles because they were formless. TG, DTG and DTA analyses of the compound were carried out, the characteristics of physico-chemical processes occurring in the N_2 environment in the range of 293 – 1223 K temperature was clarified.

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ETİLENQLİKOL MÜHİTİİNDƏ Tl_3AsS_4 BİRLƏŞMƏSİNİN ALINMASININ TƏDQİQİ

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Məqalədə etilenqlikol mühitində Tl_3AsS_4 birləşməsinin alınmasına və fiziki-kimyəvi analizinə (RFA, DTG, TG, DTA və SEM) aid nəticələr verilmişdir. Müəyyən edilmişdir ki, həlledici olaraq etilenqlikoldan və ilkin komponent kimi $TlNO_3$ və As_2S_5 birləşmələrindən istifadə etdikdə 80℃ temperaturda Tl_3AsS_4 birləşməsi alınır. Tl_3AsS_4 birləşməsi $TlNO_3$ və As_2S_5 birləşmələrinin 4:15 mol nisbətindəki qarışığında formalaşır. 80 ℃ temperaturda (pH=7-8) alınan Tl_3AsS_4 birləşməsinin tərkibində cüzi miqdarda (~ 0.02 %) sərbəst kükürd iştirak edir. Birləşməni 410 ℃ -də ikizonalı rejimdə termiki emal etdikdə təmiz şəkildə Tl_3AsS_4 birləşməsi alınır. Etilenqlikol mühitində alınmış Tl_3AsS_4 birləşməsinin mikromorfologiyası öyrənilmişdir. Müəyyən edilmişdir ki, 80℃ temperaturda Tl_3AsS_4 birləşməsinin nanohissəcikləri formalaşır. Termoqravimetrik analiz nəticələrinə əsasən Tl_3AsS_4 birləşməsi N_2 qazı mühitində T>460 ℃ olduqda parçalanır.

Açar sözlər: *differensial termoqravimetrik analiz, məhlul, mikromorfologiya, element analizi, çökmə, tritallium tetratioarsenat*

ИССЛЕДОВАНИЕ ПОЛУЧЕНИЯ Tl_3AsS_4 В СРЕДЕ ЭТИЛЕНГЛИКОЛЯ

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В статье представлены результаты получения и физико-химического анализа (РФА, ДТГ, ТГ, ДТА и СЭМ) Tl_3AsS_4 в среде этиленгликоля. Было обнаружено, что при использовании этиленгликоля в качестве растворителя, а $TlNO_3$ и As_2S_5 в качестве исходных компонентов в соотношении 4:15 мол, Tl_3AsS_4 образуется при температуре 80℃. Tl_3AsS_4, полученный при температуре 80℃ (pH = 7-8), содержит небольшое количество (~0.02%) свободной серы. При термообработке соединения при 410℃ в двухзонном режиме получается чистое соединение Tl_3AsS_4. Изучена микроморфология полученного Tl_3AsS_4. Согласно результатам термогравиметрического анализа, соединение Tl_3AsS_4 разлагается в газовой среде N_2 при T>460 ℃.

Ключевые слова: *дифференциальный термогравиметрический анализ, раствор, микроморфология, элементный анализ, седиментация, тетратиоарсенат триталлия*