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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

SYNTHESİS OF THİOSTİBİATES BY İNTERACTİON OF STİBİUM (V) SULFİDE WİTH Ag^{1+}, Cu^{1+}, Cu^{2+}, Tl^{1+} AND Sb^{3+} İONS IN AQUEOUS AND ORGANIC ENVIRONMENTS AND THEIR PHYSICOCHEMICAL STUDY

Specialty: 2303.01 – Inorganic chemistry

Field of science: Chemistry

Applicant: **Sevda Hasan Aliyeva**

NAKHCHIVAN – 2024

The dissertation work was performed in the laboratory of "Chemistry and Technology of Mineral Raw Materials" of the Institute of Natural Resourcesof the Ministry of Science and Education of the Republic of Azerbaijan.

Scientific supervisor: D. Sci. Chem.
Bayram Zulfugar Rzayev

Official opponents: D. Sci. Chem., professor
Ozbek Misirkhan Aliev

D. Sci. Chem., professor
Fuad Mikayil Sadigov

D. Sci. Chem., professor
Yasin Naghi Babayev

Dissertation Council ED 1.15 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating in the Institute of Catalysis and Inorganic Chemistry named after Acad. M.Nagiyev of the Ministry of Science and Education of the Republic of Azerbaijan

Chairman of the Dissertation council:

D. Che. Sci., academician
Dilgam Babir Tagiyev

Scientific secretary of the Dissertation council:

PhD in chemistry, associate prof.
Ulviyya Ahmed Mammadova

Chairman of the Scientific Seminar:

D. Che. Sci., prof.
Akif Shikhan Aliyev

GENERAL DESCRIPTION OF WORK

Relevance and degree of investigation of the topic. The rapid development of modern technology in the XXI century is mainly related to the production of semiconductor materials. Works carried out in the field of nanoparticle synthesis play an important role in achieving new results in microelectronics. Taking into account the wide use of binary and ternary semiconductor compounds in technology, a certain degree of demand has arisen in the direction of developing the methods of micro and nanoparticle synthesis, the elaboration of simple and available methods of obtaining nanocomposites and thin films. The study of the structure and physical-chemical properties of compounds with various components attracts the attention of scientists in most countries. The obtaining of micro- and nano-sized, nanoporous materials with different properties leads to the creation of new production areas.[1]

Stibium ternary sulfides are used in industry to synthesize heterogeneous nanocatalysts and efficient gas storage materials. Another important application field of nanomaterials is their use as adsorbent materials. Currently, various industrial nanofilters and nanofibers are prepared based on organic polymers. Porous adsorbents are produced from sulfur-based inorganic nanomaterials in some industries. For example, layers of thiol-bonded organic molecules on the pore walls composed of mesoporous silica are used to remove lead and mercury from water. Over the past two decades, various metal sulfidenanomaterials have been developed, and studies have shown that their physical properties depend on the size and shape of the materials.[2]

One of such materials are compounds obtained based onantimonysulfides. Sb_2S_5 with its attractive photoconductive properties and high thermoelectric properties has wide industrial

[1]Hüseynov Q. Darıdağ sürmə filizi əsasında AgSb1-xS tərkibli üçlü sulfidlərin hidrokimyəvi çökdürülməsi tərkib və xassələrinin araşdırılması / AMEA Naxçıvan Bölməsi Elmi Əsərlər. Təbiət və texniki elmlər seriyası 2022, № 2, s.34-39.

[2]G.M.Hüseynov, N.Ə.Məmmədova, H.Ə.İmanov, Tioasetamid və antimon (III) xlorid əsasında nanoölçülü Sb_2S_3 tərkiblərinin alınması / Kimya Problemləri № 3 2017 s.329-334

applications as a targeted material for television cameras, microwave devices, switching, and optoelectronic devices.

Some physical properties of Sb_2S_5, such as photoelectric properties and carrier transport conductivity of mechanisms, are available in the literature[3].

In recent years, the production of photovoltaic cells, solar cells, and photoelectrochemical cells has increased sharply due to the increasing demand for renewable energy sources. The electrical properties of semiconductors depend on their chemical composition and structural properties. Many compounds with different properties have been obtained as a result of the development of nanoscale and nanoporous materials by increasing the surface area[4]. For example, their use as industrial heterogeneous nanocatalysts, efficient gas storage materials, and adsorbents. The above shows the relevance of the dissertation work.

Object and subject of research. The ternary thio-compounds obtained in solution from the interaction of sodium thiostibiate with Cu^{1+}, $Cu^{2,+}$ Ag^{1+}, Sb^{3+} salts, as well as from the reactionproceeding between stibium (V) sulfide and Cu^{1+}, $Cu^{2,+}$ Ag^{1+}, Tl^{1+} salts were the object of the study. To carry out the research, stibium (III) sulfide obtained by sublimation from Daridagstibium ore was used as the starting material. Antimony (V) sulfide is obtained from sodium thiostibiate, which is obtained based on antimony (III) sulfide.The physico-chemical properties of thio-compounds obtained based on these compounds were studied and their fields of use were determined. Studying the conditions for obtaining stibiumthio-compounds in solution by the interaction of copper, silver, thallium, and antimony salts with Na_3SbS_4 and Sb_2S_5 was the research subject.

The aim and tasks of the study. The dissertation work aims to study the condition for obtaining stibiumthio-compounds in

3G.M.Hüseynov, N.Ə.Məmmədova, H.Ə.İmanov, Tioasetamid və antimon (III) xlorid əsasında nanoölçülü Sb2S3 tərkiblərinin alınması / Kimya Problemləri № 3 2017 s.329-334

[4]Yang R.B., Liquid-Solid Growth of Antimony Selenide and Antimony Sulfide Nanowires / Bachmann, P.E, Berger A J, Woltersdorf J, Goesele U, [et.ac/] // Advanced Materials 17 avqust p.3170-3174

solution by the interaction of copper, silver, thallium, and stibium salts with sodium thiostibiate and stibium(V) sulfide, and to determine their physical and chemical properties.

In accordance with the aim of the study, the following tasks were resolved:

- Obtaining Na_3SbS_4 from stibium (III) sulfide;
- Study of the condition for obtaining silver thiostibiate, copper (I) thiostibiate, copper (II) thiostibiate and stibiumthiostibiate from sodium thiostibiate;
- Synthesis of copper (I) thiostibiate from Sb_2S_5-CuCl-H_2O system;
- The obtaining thallium thiostibiate from stibium (V) sulfide and thallium nitrate;
- Study of the condition for obtaining silver (I) thiostibiate from Sb_2S_5-$AgNO_3$-H_2O system;
- Synthesis of copper (I) thiostibiate bysolvothermal method;
- Study of the condition for the synthesis of silver (I) thiostibiatebysolvothermal method;
- Study of the condition for the synthesis of thallium (I) thiostibiateby solvothermal method

Methods of the research. The research on the dissertation work was carried out using differential thermal (DTA), thermogravimetric (TQ), X-ray phase (XRD), elemental, calorimetric, ultraviolet (UV) spectroscopy and scanning electron microscopy (SEM) analysis methods, which are of great importance in modern times for physical and chemical analysis. Differential thermal, and thermogravimetric analyses of the synthesized samples were carried out on a NETZSCH STA 449F3 device. In addition, a Thermoscan-2 device was also used for DTA. X-ray phase analysis of the obtained thiocompounds was performed on a D2 PHASER "Bruker" (CuK_α, 2θ, 20-80 degrees) diffractometer. A HITACHI TM 3000 scanning electron microscope was used to examine the morphology and structure of the samples. Both the qualitative and quantitative composition of the compounds was determined on a JSM-6610LV SEM-Oxford Instrument elemental analysis device.

Provisions submitted for defense

- Conditions for obtaining sodium thiostibitate;
- Results of the study of the systems Sb_2S_5-CuCl-H_2O, Sb_2S_5-$AgNO_3$-H_2O, Sb_2S_5-$TlNO_3$-H_2O
- Results of the synthesis of Cu_3SbS_4, Ag_3SbS_4, Tl_3SbS_4 and $SbSbS_4$thiostibiate compounds of stibium (V) sulfide by the solvothermal method
- Physicochemical properties of Cu (I), Cu (II), Tl (I), and Ag (I) sulfosalts synthesized in aqueous and organic media.

Scientific novelty:

The following scientific results were achieved in the dissertation work:

- Preparation of sodium thiostibiate from Darıdag antimony ore
- The conditions for the preparation of Cu_3SbS_4, Ag_3SbS_4, and $SbSbS_4$ metal thiostibites from sodium thiostibite solution were studied.
- Stibium penta sulfide was synthesized by a screen printing method.
- Methods for obtaining ternary thiocompounds from the interaction of stibium penta sulfide with copper (I) chloride, copper (II) chloride, silver nitrate, and thallium nitrate in the aqueous medium were determined and the synthesized compounds were extensively studied.
- The corresponding ternary thiocompounds were synthesized from the interaction of stibium penta sulfide with silver nitrate, copper (I) chloride, copper (II) chloride, and thallium nitrate in an organic medium, and their nano and microparticles were obtained

The theoretical and practical significance of the research. The study of the conditions for obtaining ternary thiocompounds from the interaction of sodium thiostibitate and antimony (V) sulfide with water-soluble salts of Cu^{1+}, Cu^{2+}, Ag^{1+}, Tl^{1+}, Sb^{3+} in solution, the development of a new, simpler synthesis method compared to the high-temperature synthesis method, and the results obtained on the physicochemical properties of the obtained antimony (V)

thiocompounds are included in the group of ternary metal chalcogenides and make a significant contribution to materials science.

The practical significance of the dissertation work lies in the fact that the methods for obtaining thiocompounds synthesized from the Me^{n+}-Sb_2S_5 (Me^{n+}=Cu^{1+}, Cu^{2+}, Ag^{1+}, Tl^{1+}, Sb^{3+}) system in water and organic media are very simple, carried out under ordinary conditions and at relatively low temperatures (20-120℃), do not require complex devices, expensive reagents, and easy conditions for conducting experiments. Such a method of obtaining samples can be used in the preparation of nanostructures. Sodium antimony sulfide, antimony (III) sulfide, and ternary thiocompounds synthesized based on Cu^{1+}, Ag^{1+}, Tl^{1+} and Cu^{2+} are used as semiconductor materials in sodium-ion batteries, nonlinear optical devices, optical fiber production, preparation of parts of optical devices, in video-technics and microelectronics, as a receiving surface in solar cells, optoacoustic devices, chemical sensors and promising photo and ferroelectric materials, such as solid electrolytes, electrochemical sensors, electrochemical screens, etc. We believe that thiocompounds synthesized from theMe^{n+}-Sb_2S_5 (Me^{n+}=Cu^{1+}, Cu^{2+}, Ag^{1+}, Tl^{1+}, Sb^{3+}) system can also be used in the mentioned application areas. At the same time, the $SbSbS_4$ compound has practical importance as an additive to high-temperature lubricants.

Approbation and application of the work. The main results of the thesis were discussed at the following conferences: "Current problems of modern chemistry" International Scientific Conference dedicated to the 90th anniversary ofInst. of Petrochemical Processes of ANAS (Baku/Azerbaijan, October, 2-4, 2019), Second International Scientific Conference of Young Scientists and Specialists (Baku/Azerbaijan, March, 3-6, 2020), Endless Light in Science, Kazakhstan (Almaty, Kazakhstan, March 20, 2023), Materials of the XLVII International Scientific-Practical Conference (Krakow, Poland (remote) August 7, 2024), Collection of Scientific Papers based on the results of an XXIV international scientific conference (France, Lyon, 15 July 2024).

9 articles, 6 of which are unco-authored, (1 article in the Web of Science and 2 articles in the CAS index database) and 8 conference materials have been published in local and international indexed journals. Published scientific articles and theses completelyinvolve the content of the dissertation.

The name of the organization in which the work was carried out. The dissertation work was carried out in the laboratory "Chemistry and technology of mineral raw materials" of the Institute of Natural Resources, Ministry of Science and Education of the Republic of Azerbaijan.

The author's personal contribution. The author directly participated in the selection of the dissertation topic and the solution of the issues, together with his scientific supervisor. The samples were synthesized by the author in the laboratory at low temperatures (105-70℃) in various chemical containers. Solving the issues posed in the dissertation work, conducting experimental research, performing analyses based on the samples obtained from laboratory experiments, and analyzing the results were carried out by the author, the results were discussed with scientific supervisors and scientific articles were prepared.The research results were reported at scientific conferences at the international and national levels.

The total symbolic volume of the dissertation. The dissertation consists of an introduction, 5 chapters, a conclusion, and a review of the used references. The work contains 168 pages including 56 figures, 32 tables, and 147 reference materials. The total volume of the work (excluding tables, graphs, figures, and bibliography) consists of 196 310 characters.

THE MAIN CONTENT OF THE WORK

In the **first chapter** of the dissertation, the results of scientific research conducted on the Na-Sb-S, Sb-S, Ag-Sb-S, Tl-Sb-S, Cu-Sb-S, Sb-Sb-S systems, the conditions for obtaining binary and ternary compounds synthesized from these systems, and the literature materials that record the physicochemical properties of these compounds were analyzed and systematized.

The **second chapter** of the work contains information about chemically pure reagents used for laboratory experiments, chemical analysis methods, physicochemical analysis methods, devices used for experiments, and their working principles.

The **third chapter** describes the interaction characteristics of sodium thiostibite with silver nitrate, copper (I), copper (II) chloride, and antimony salts and the results of the physicochemical analysis of the synthesized thiocompounds. The individuality of the samples of the compounds obtained from sodium thiostibite and Ag^{1+}, Tl^{1+}, Cu^{1+}, Sb^{3+} was confirmed by XRD, DTA, TG, SEM, and elemental analysis methods. A chemical analysis of the obtained samples was carried out. The Ag^{1+}, Cu^{1+}, Sb^{3+} ions in the samples were determined by faience and barometric methods. All compounds were obtained in an acidic medium in the pH range of 1-4. The results of differential thermal analysis of the obtained compounds by DTA (Thermoscan2) showed that the compounds are stable up to a temperature of 625 ℃. To clarify the stoichiometric composition of these compounds, elemental analysis of the composition of the obtained compounds was carried out. The composition of the thiostibitate precipitates was studied using the XRD phase (2D PHASER "Bruker") analysis method.

Synthesis of sodium thiostibite compound. Sodium thiostibite is also called Schlippe salt. As a startingmaterial, antimony (III) sulfide was obtained from Darıdag antimony ore. After dissolving antimony (III) sulfide in concentrated hydrochloric acid, it was purified from impurities by distillation [5, p. 52]. Hydrogen sulfide was released from the antimony (III) chloride solution at room temperature and the solution turned orange. Hydrogen sulfide gas was released until complete precipitation occurred. Then, chemical antimony (III) sulfide was filtered through filter paper until chloride and sulfide ions were removed. Then, it was washed with ethyl alcohol, dried, and prepared to obtain Schlippe salt. Other components were chemically pure sodium hydroxide and elemental sulfur.

The reaction equation for obtaining sodium thiostibite is formulated as follows:

$$Sb_2S_3 + 8NaOH + 6S = 2Na_3SbS_4 + Na_2SO_4 + 4H_2O \quad (1)$$

The substances, taken in stoichiometric proportions according to the reaction equation, are mixed and heated to boiling. The heating continued with periodic addition of water to the mixture. After the dissolution was complete, the solution was filtered, and after some evaporation, the filtrate was left to crystallize. The obtained crystals were filtered through a Buchner funnel and dried in a vacuum at room temperature. The crystals acquire a grayish-white color. To study the physicochemical properties of the sample, its thermogravimetric analysis was initially conducted. The results of the analysis are presented in Figure 1 [5, p. 52].

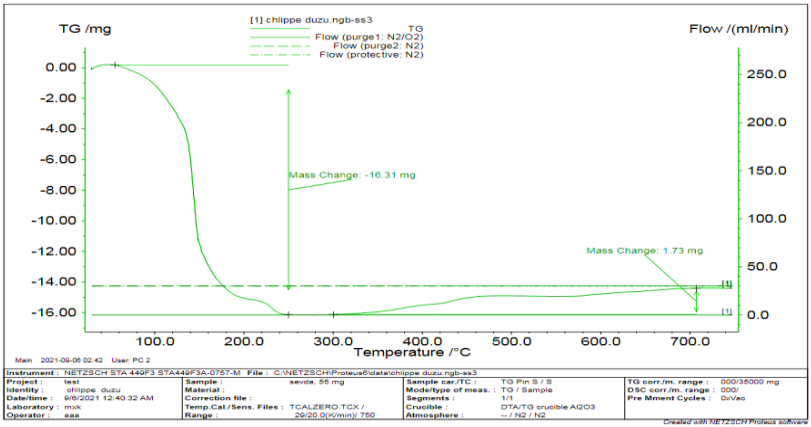


Figure 1. Thermogram of sodium thioantimonate [5, p. 52]

As seen from the thermogram, the first mass loss continues to increase, starting at approximately 90-100℃, and finally stabilizes at a temperature of 240℃. The mass loss at this temperature was 16.31 mg. This corresponds to the crystallization water. Theoretically, the amount of crystallization water in the taken sample (55.0 mg) should be 17.25 mg. Calculations have shown that the amount of crystallization water in the sample is approximately 8.8-9.0 moles. It fluctuates around this value. The residue after dissolving in water was acidified with hydrochloric acid. At this time, antimony (V) sulfide precipitates from the solution. The mass of Sb_2S_5 was

determined, and it was found that sodium thioantimonate does not decompose.

Synthesis of silver thiostibitate compound from sodium thiostibitate. In the experiments, 0.1M solutions of sodium thiostibitate ($Na_3SbS_4 \cdot 9H_2O$) and 0.1M solutions of silver nitrate were used. Silver nitrate solution is added to the sodium thiostibitate solution and a light brown precipitate is obtained. The initial pH of the reaction is in the range of 11-12. When silver nitrate is added to the sodium thiostibitate solution, the pH of the medium changes, and the equilibrium is disturbed. The concentration of hydrogen ions in the medium is adjusted to pH 2-3. The solution is stirred for 5-7 minutes. The obtained precipitate is filtered, washed first with distilled water, then with ultrapure water, and dried at a temperature of 105℃ to a constant mass. After the process was completed, it was determined that there were no silver ions in the filtrate. At this time, silver ions were included in the composition of the compound. The compositional analysis of the obtained sample showed that the compound contains all three antimony, silver, and sulfur ions. At the same time, the absence of antimony ions in the filtrate not only indicates that the process proceeds according to the reaction equation below, but also allows us to monitor the completion of the process [6, p. 60].

$$Na_3SbS_4 + 3AgNO_3 \rightarrow Ag_3SbS_4\downarrow + 3NaNO_3 \qquad (2)$$

The precipitate quickly separates from the solution, which facilitates the filtration of the solution. Under the established optimal conditions, thermogravimetric, X-ray phase, and chemical analyses of the obtained compound were performed. Based on the results of the chemical analysis, it was determined that the formula of the obtained compound corresponds to Ag_3SbS_4. The density of Ag_3SbS_4 was determined by the pycnometric method. The chemical method was used to study the sample's resistance to acids and alkalis. The values of the thermodynamic parameters of the reaction were calculated.Thermogravimetric analysis of the synthesized silver thioantimonate salt was conducted (Fig. 2).

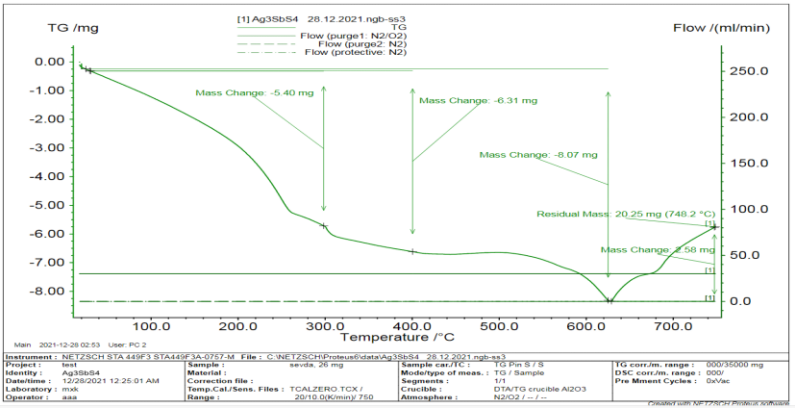


Figure 2. The thermogram of Ag_3SbS_4 [6, p. 63]

As can be seen from Figure 2, the compound was heated to 1023 K in an air oxygen environment (air supply rate 30 ml/min). In general, the mass of the sample at a temperature of 300℃ decreased by 5.40 mg. According to theoretical calculations, sulfur in a 26 mg sample (Ag_3SbS_4) is 5.65 mg. Since the experimentally determined mass loss corresponds to this value, it can be said that this loss is sulfur. The subsequent mass loss was due to the oxidation and sublimation of antimony. Thus, in the temperature range of 300-600℃, a part of antimony (2.67 mg) is converted into antimony (III) oxide and expelled. The other part, as the temperature increases, is converted into antimony (V) oxide and remains in the residue. A 26 mg sample theoretically contains 5.51 mg of antimony, and it is known that it is (5.51-2.67= 2.84 mg) and 14.68 mg of Ag. Thus, the total of the oxides formed by 2.84 mg of antimony and 14.68 mg of Ag is 19.45 mg. Experimentally, the residue was 20.25 mg, which is approximately consistent with each other. At the same time, the residue was also chemically analyzed, and the results obtained were consistent with the mass of the residue [6, p. 63].

Preparation of copper (I) thiostibite from sodium thiostibite. In the experiments, a solution of 0.1M sodium thiostibite and 0.1M copper (I) chloride in ammonium hydroxide was taken and mixed. As a result of the reaction, a brown precipitate was formed, but the precipitate did not separate from the solution. The initial pH of the sodium thiostibite solution was in the range of 10-11. The pH

of the solution was gradually reduced to 3-4. The solution was stirred for 7-10 minutes. The precipitate obtained was filtered, washed first with distilled water and then with ultrapure water, and dried at 105℃ to a constant mass [11, p. 31].

The results of the initial chemical analysis of the composition of the sample obtained showed that the compound contains all three antimony, copper, and sulfur ions. At the same time, the absence of antimony ions in the filtrate not only indicates that the process proceeds according to the reaction equation below, but also allows us to monitor the completion of the process.Thermal analysis of the obtained thiosalts was performed and the results are shown in Figure

$$Na_3SbS_4 + 3CuCl \rightarrow Cu_3SbS_4\downarrow + 3NaCl \qquad (3)$$

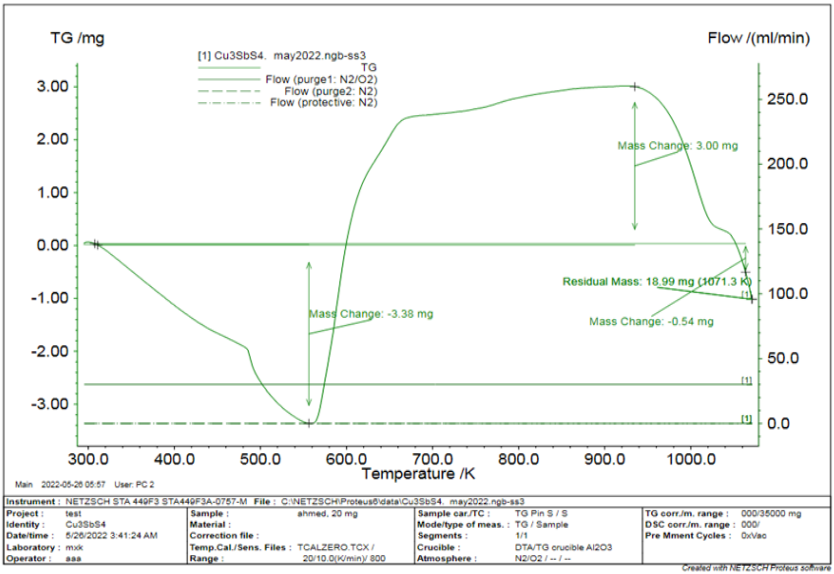


Figure 3. The thermogram of Cu_3SbS_4 [11, p.30]

As can be seen from Figure 3, the compound was heated to a temperature of 1100℃ in an atmosphere of air oxygen (air supply rate 30 ml/min). According to theoretical calculations, sulfur in a 20 mg sample (Cu_3SbS_4) is 5.79 mg. [15, p. 64]

Experimentally, since the mass of the sample at a temperature of 300℃ K decreased by 3.38 mg, it can be said that this loss was

sulfur. At subsequent temperatures, the mass of the sample increased. Thus, in the temperature range of 827-940℃, it was due to the oxidation of antimony and copper. It was determined that the mass loss of 3.38 mg (theoretical mass of sulfur is 5.79 mg) was due to sulfur belonging to antimony. Sulfur corresponding to copper was converted into copper (II) sulfate during oxidation [11, p. 30].

$$CuS + 2O_2 = CuSO_4 \quad (4)$$

At temperatures between 567-927℃, copper (II) oxide was obtained from the decomposition of copper (II) sulfate.

$$2CuSO_4 \rightarrow 2CuO+2SO_2+ O_2 \quad (5)$$

Theoretically, the total mass of the oxides formed by antimony and copper in the sample is 19.14 mg (fig.3). The mass of the residue formed experimentally was 18.99 mg, which is approximately equal to each other. At the same time, the residue was also chemically analyzed, and the results obtained were consistent with the mass of the residue.

Preparation of antimony thiostibitate from sodium thiostibitate.

Sodium thioantimonate was obtained in the laboratory by sublimation (purity grade 10-20%) from antimony ore through the interaction of pure antimony (III) sulfide, free sulfur, and sodium hydroxide. The salt antimony-potassiumantimonyl tartrate was obtained from antimony (III) chloride, which was produced by distilling the same antimony (III) sulfide dissolved in hydrochloric acid.

Na_3SbS_4 is poured into a 100 ml laboratory beaker and a solution of potassium antimony nitrate is prepared in another test vessel. After the solutions are prepared, the potassium antimony nitartrate solution is added in portions to the sodium thiostibite solution under a pH meter. 0.1 N HCl is used to reduce the pH of the mixture. The reaction equation for the process is formulated as follows:

$$Na_3SbS_4+KSbOC_4H_4O_6 +3HCl=SbSbS_4\downarrow+KHC_4H_4O_6+ +3NaCl+H_2O \quad (6)$$

It can be seen from the reaction equation that no intermediate products are formed during the process. Antimony thiostibite and potassium antimony nitrate precipitate and separate from the solution,

At the beginning of the reaction, the pH of the medium of both solutions is equalized. After the process is completed, the pH of the medium is adjusted to 3-4 and filtered through a glass filter. To separate the potassium antimony nitrate from the precipitate, it is first washed with weak hydrochloric acid, then washed with distilled water and ethyl alcohol, and dried at a temperature of 624℃ [8, p. 57].

Thermogravimetric analysis of the sample was performed. The results of the analysis are shown in Figure 4.

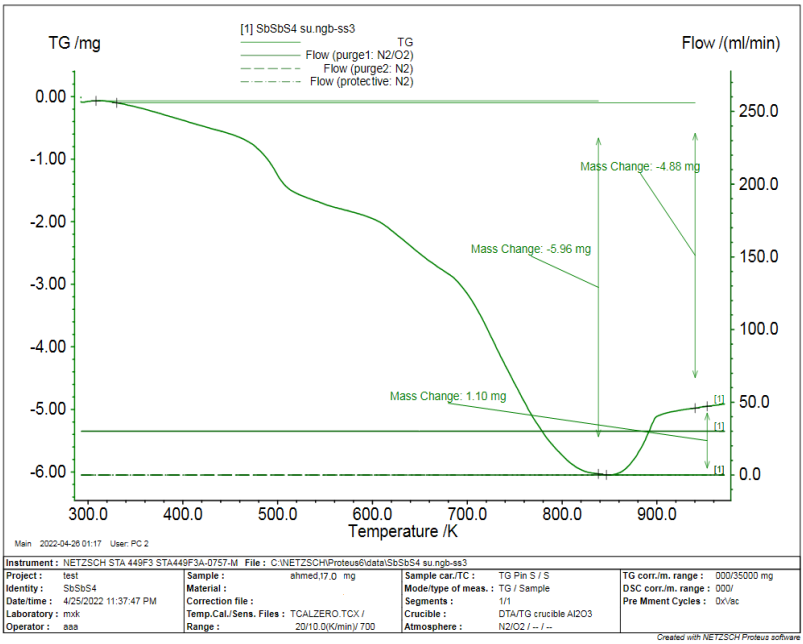


Figure 4. The thermogram of stibium thiostibitate [8, p. 57]

Theoretically, it is known that 17.0 mg of antimony thiostibite contains 11.15 mg of antimony and 5.85 mg of sulfur. As can be seen

from the figure, there was a mass loss of 5.96 mg up to a temperature of 850℃. At this temperature, only sulfur can be removed. This mass loss is 96% of sulfur. Above 577℃, antimony oxidizes to antimony (III) and (V) oxides and is not removed. This is clearly seen from the curve. In general, 11.20 mg of antimony and 5.96 mg of sulfur were found in the sample. This is in agreement with the theoretical amounts. The obtained result confirms that the sample is antimony antimony thiostibite. XRD phase analysis of the sample was performed. The obtained results are given in Figure 5. The results of the analysis confirm the individuality of antimony (V) sulfide, which has an amorphous structure [8, p. 57].

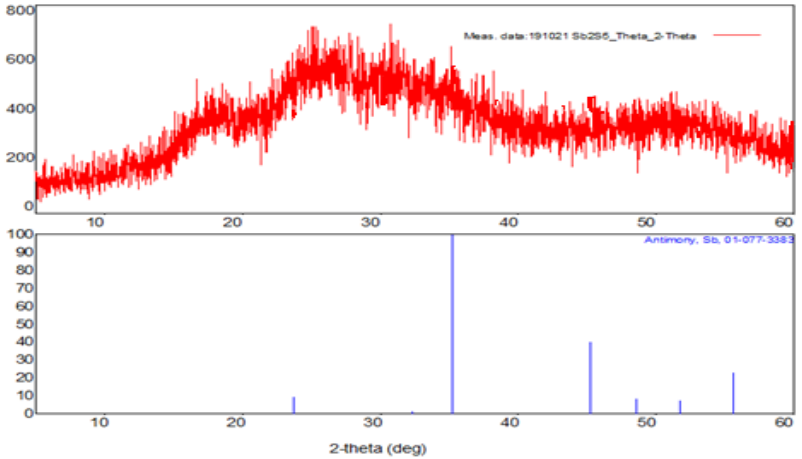


Figure 5. XRD analysis of stibium stibite [8, p.58]

Obtaining the corresponding thiostibites from the interaction of Cu^{1+}, Cu^{2+} ions with antibium penta sulfide: The copper (I) chloride used in the experiments was obtained in the laboratory in the presence of $CuSO_4$, NaCl, and Na_2SO_3. Since copper (I) chloride is insoluble in water, its 0.1 M solution was prepared in ammonium hydroxide. Orange-red antibium (V) sulfide was obtained from the decomposition of a certain concentration of sodium thiostibitate in an acidic medium. Antibium (V) sulfide was prepared for the experiment by washing it first with distilled water and then with ultrapure water. The determination of antibium ions

not only shows that the process proceeds according to the reaction equation below, but also allows you to control the completion of the process [16, p. 228].

$$4Sb_2S_5+15CuCl+12H_2O=5Cu_3SbS_4+15HCl+3H_3SbO_4 \quad (7)$$

The investigation of the conditions for obtaining silver(I) thiostibite from the Sb_2S_5-$AgNO_3$-H_2O system. A blackish-brown precipitate is obtained by adding silver nitrate solution to a sample of stibium (V) sulfide. The precipitate was then filtered, washed, and dried at 105 ℃. It was observed that silver ions were present in the filtrate. The preparation of silver thiostibite from stibium (V) sulfide proceeds according to the following reaction [14, p. 30].

$$4Sb_2S_5+15AgNO_3+12H_2O=5Ag_3SbS_4+15HNO_3+H_3SbO_4 \quad (8)$$

X-ray diffraction analysis of the obtained compound was performed before and after thermal treatment (Fig. 6). According to the analysis of the obtained results, it was found that the formula of the compound after thermal treatment is $Ag_3SbS_3(S_4)$. The fact that the composition of the precipitate obtained during the precipitation process corresponds to Ag_3SbS_4 is also confirmed by literature sources. Thus, as shown in the literature review of the dissertation work, this compound is formed as Ag_3SbS_3 and is stable up to 600 ℃. When the compound is heated, sulfur decomposes with separation and turns into silver thiostibitate, which is confirmed by the results of XRD analysis [12, p.24]. Thus, if antimony (V) sulfide is taken initially, the obtained compound corresponds toantimony (III) sulfide. It seems that during the reaction, an intramolecular oxidation-reduction process occurs and $Sb^{5+}\rightarrow Sb^{3+}$ is reduced. The reduction process occurs due to one of the sulfur atoms in Sb_2S_5.

$$Ag_3SbS_4 \rightarrow Ag_3Sb_2S_3 + S^0 \downarrow$$

$$Sb^{+5} + 2e^- \rightarrow 2Sb^+$$

$$S^{-2} - 2e^- \rightarrow S^0$$

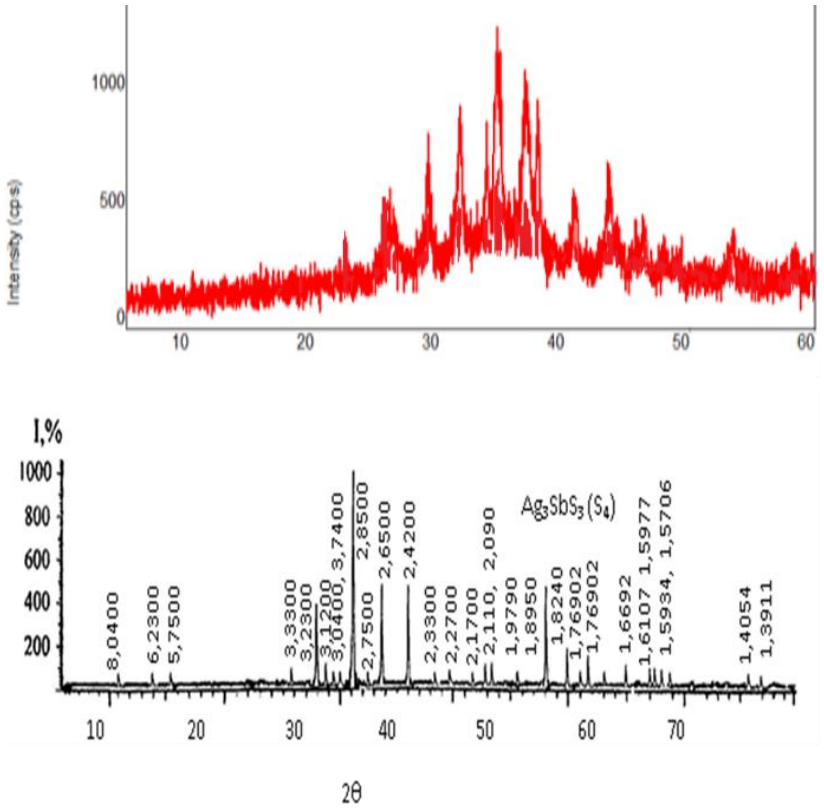


Figure 6. Diffractogram of Ag_3SbS_4 before (a) and after (b) thermal treatment [12, p.24]

At the same time, it was determined by XRD analysis that the crystallization degree of the Ag_3SbS_4 compound obtained in an aqueous medium is 65.2%.

Preparation of thallium thiostibitate from antimony (V) sulfide and thallium nitrate

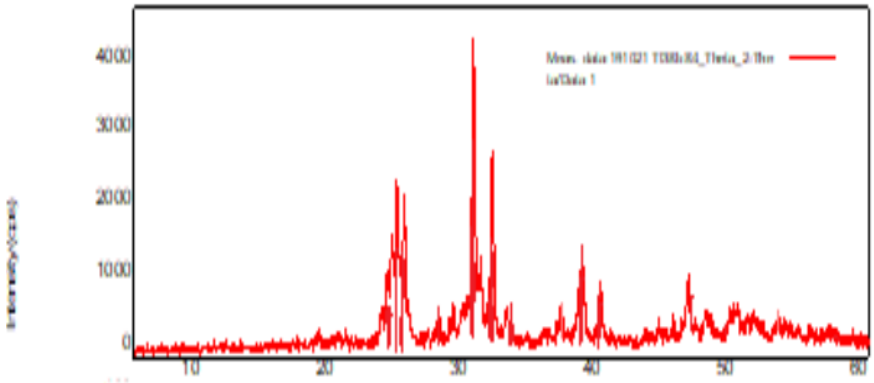
Chalcogenides of p-elements are among the promising materials for electronics. In particular, chalcogenides of bismuth and antimony, as well as solid solutions based on them, are thermoelectric materials that can be used in the temperature range of

77-85℃. These materials are used in both cooling and thermoregulating devices, as well as in thermoelectric generators.

A 0.1 M solid solution of thallium nitrate was prepared, which will be used during the work. Orange-red antimony (V) sulfide was obtained by hydrolysis of sodium thiostibitate of a certain concentration in an acidic medium. Antimony (V) sulfide was prepared for the experiment by washing it first with distilled water and then with ultrapure water. A thallium nitrate solution corresponding to the stoichiometry is added to a known amount of antimony (V) sulfide sample and mixed. At this time, the color of the orange antimony (V) sulfide turns blackish brown. The resulting precipitate is filtered, washed first with distilled water and then with ultrapure water, and dried at a temperature of 105℃ to a constant mass. After filtering the mixture, the antimony (V) ions in the filtrate were examined and it was determined that there was antimony. The results of the compositional analysis of the resulting compound showed that all three antimony, thallium, and sulfur ions were present in the compound. At the same time, as mentioned above, the presence of antimony ions in the filtrate also indicates that the process occurs according to the reaction equation below [7, p. 43].

$$4Sb_2S_5+15TlNO_3+12H_2O=5Tl_3SbS_4+15HNO_3+3H_3SbO_4 \quad (9)$$

XRD analysis of thallium thiostibitate was performed and its diffractogram was recorded (Fig. 7). At the same time, XRD analysis determined that the degree of crystallization of the compound Tl_3SbS_4 obtained in an aqueous medium is 67.2%.



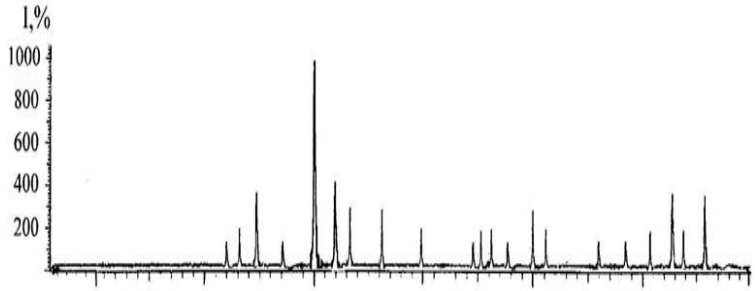


Figure 7. X-ray diffraction pattern of the Tl_3SbS_4 compound before (a) and after (b) technical processing [7, p.43]

According to the values obtained as a result of the analysis, it was found that the formula of the compound was $TlSbS_3$-Tl_2S. $TlSbS_3$-(PDF -00-028 -1024). Thus, while the amounts of antimony (V) sulfide and $TlNO_3$ were initially taken according to the formula Tl_3SbS_4, the resulting compound corresponded to $TlSbS_3$–Tl_2S. It seems that an intramolecular transformation occurred during the reaction.

$$Tl_3SbS_4 \leftrightarrow TlSbS_3 + Tl_2S \qquad (10)$$

Study of the conditions for obtaining antimony (V) sulfide by the solvothermal method. Experiments on antimony (V) sulfide in a non-aqueous medium were performed in the following sequence. 15-20 ml of ethylene glycol is poured into a 50 ml round-bottomed flask, and antimony salt -Na_3SbS_4 is added to it and mixed. After the salt dissolves, a certain amount of ammonium chloride is added to the experimental flask. The mouth of the experimental flask is closed and placed in an oven at a temperature of 150℃. The process duration is selected as 8-10 hours, and during this time the sample is kept in the oven. The progress of the experiment is monitored every 2 hours. After the first 2 hours, a dark red precipitate begins to separate from the solution. Over time, it is felt that the amount of precipitate increases. After the end of the process, the solution is cooled diluted, and filtered through a glass filter. The precipitate is

first washed with distilled water and then with ethyl alcohol and dried at 110℃ [16, p. 226].

Based on the results obtained, the mass and atomic ratios of antimony and sulfur in the compounds were determined. Based on the results of elemental analysis, the simple formula of the compound obtained in ethylene glycol was determined to be Sb_2S_5. The micromorphology of the Sb_2S_5 compound obtained in ethylene glycol at a temperature of 150℃ was studied with a HITACHI TM3000 microscope (Fig. 8).

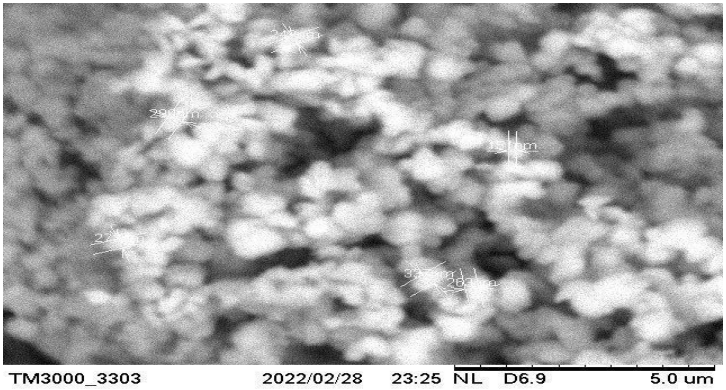


Figure 8. The SEM image of antimony (V) sulfide obtained in ethylene glycol [16, p.228]

Solvothermal synthesis of copper (I) thiostibitate. This subsection describes the conditions for obtaining nanoparticles of the Cu_3SbS_4 compound in a mixture of ethylene glycol (EG) and polyethylene glycol (PEG) by the solvothermal method.

The chemical reagents used for the synthesis of copper-stibium-sulfide nanoparticles were ethanol, distilled water, ultrapure water, Becton-copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 99.99%), elemental sulfur (99.998%), ethylene diamine, potassium antimonyl tartrate, ethylene glycol, and polyethylene glycol. N-heptane was used to prepare the dispersed solution of nanoparticles. The synthesis of Cu_3SbS_4 was performed as follows. Amounts of Cu(II) chloride and potassium antimonyl tartrate were taken in stoichiometric ratios and dissolved in an organic mixture (EG+PEG). In another test tube,

elemental sulfur was dissolved in ethylenediamine to prepare a clear solution. Both solutions were transferred to the test tube and mixed with a magnetic stirrer for several minutes. Then the mixture was collected in a 50 ml Teflon cuvette and tightly closed. The volume of the final solution should be 80% of the cuvette volume. The Teflon cuvette was kept in a heater at 160℃ for 15 hours. Then the heater was allowed to cool and cooled to room temperature. The resulting nanoparticles were washed with ethyl alcohol and centrifuged (Heraeus Thermo Scientific). The centrifuged products were collected, washed with ethyl alcohol, and then dried in a vacuum at 110℃ for one hour. Physical and chemical analyses of a certain amount of copper thiostibitate samples obtained under the specified optimal conditions were performed. The morphology of the sample was studied with a scanning electron microscope (Fig.9) [13, p. 309].

A certain amount of copper thiostibitate was dispersed in 20 ml of n-heptane and its optical properties were studied. The absorption spectrum of the solution in 1 cm cuvettes was recorded on a U-5100 Hitachi ultraviolet spectrophotometer, the optical absorption curve was shown and the dependences were constructed (Figs. 10, 11).

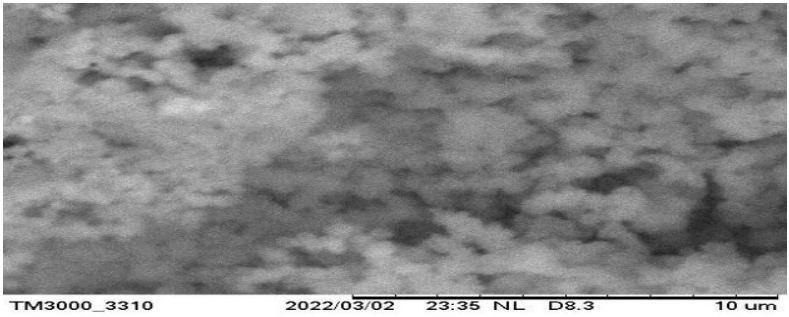


Figure 9. Micromorphology of fematite - Cu_3SbS_4, growth limit 5um[13, p.309]

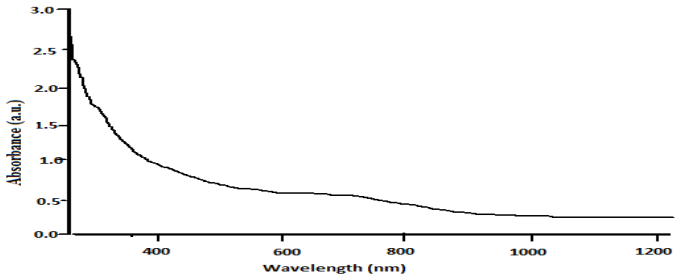
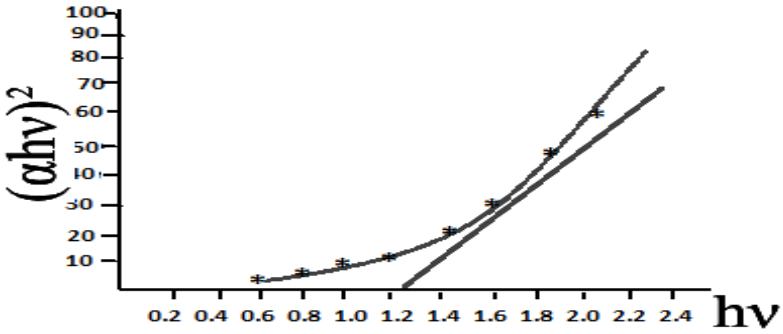


Figure 10. The absorption spectrum of a dispersed solution of copper



thiostibitate [13, p. 309]

Figure 11. Dependence of Ag_3SbS_4 - nanoparticles $(\alpha h\nu)^2$- hν (photon energy) [13, p. 310]

As can be seen from the graph, the band gap width of the Cu_3SbS_4 nano compound synthesized by the solvothermal method is equal to Eg=1.25eV. In the literature, the band gap width of the fematinite thin layer takes different values (0.85-1.20eV) depending on the conditions of its preparation.

Investigation of the conditions for the synthesis of silver thiostibitate by the solvothermal method The experiments were carried out in the following order: 0.25 g of sodium thiostibitate crystal hydrate ($Na_3SbS_4 \cdot 9H_2O$) was dissolved in an organic medium

(ethyleneglycol+polyethyleneglycol, dimethylformamide+ triethanolamine) in a ratio of 1:1.

Silver nitrate, suitable for the reaction, is also dissolved in the same mixture to some extent. Both solutions are mixed in a test vessel. The mixture is stirred with a magnetic stirrer at a temperature of 120℃ for 30-40 minutes. Then the mixture is collected in a Teflon cuvette, tightly closed, and placed in a microwave oven. The sample is heated in an oven at a temperature of 160℃ for 18 hours. After the process is completed, the precipitate obtained is filtered and washed first with distilled water and then with ethyl alcohol. The purified precipitate is dried in a vacuum at a temperature of 110℃. Preliminary analyses confirmed the presence of all three elements in the sample.

The reaction equation of the process is formulated as follows.

$$Na_3SbS_4 + 3AgNO_3 \rightarrow Ag_3SbS_4 + 3NaNO_3 \quad (11)$$

The main component of the compound obtained in an organic medium was the silver thiostibite compound. These compounds are mainly in an amorphous state. The micromorphology of the silver thiostibite compound obtained at a temperature of 160℃ was studied under an electron microscope (Fig. 12).As can be seen, the width of the forbidden zone of the compound is in full agreement with the data in the literature.

The results of SEM analysis showed that the diameters of the synthesized Ag_3SbS_4 nanorods vary between 150 and 300 nm, and their lengths reach several micrometers.

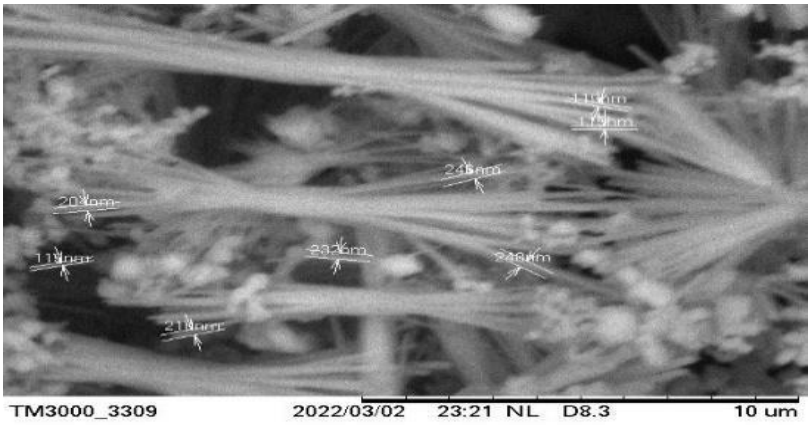


Figure 12. Microphotograph of the silver thiostibitate compound

It is known that the band gap of solutions and thin layers of semiconductor compounds can be calculated using the Tauch formula (Fig. 13).

Based on the formula, the values of $(\alpha h\nu)^2$ and $h\nu$ were calculated, and based on the obtained values, a dependence curve of $(\alpha h\nu)^2$ on $h\nu$ was constructed, and the value of the band gap of the compound was determined (Fig. 14).

SEM analysis of the Ag_3SbS_4 compound was carried out (Fig. 15) and it was determined that when the solvents changed, the shape of the particles also changed. The particles were arranged in the form of hexagonal layers. The thickness of the layers was in the range of 250-500 nm. The size of the edges of the hexagon was in the range of several microns. It was determined by experiments that no other changes occurred in the properties of the compound. The shapes of the nanoparticles were different.

$$(\alpha\hbar\nu)^{\frac{1}{n}} = A(\hbar\nu - E_g) \qquad (12)$$

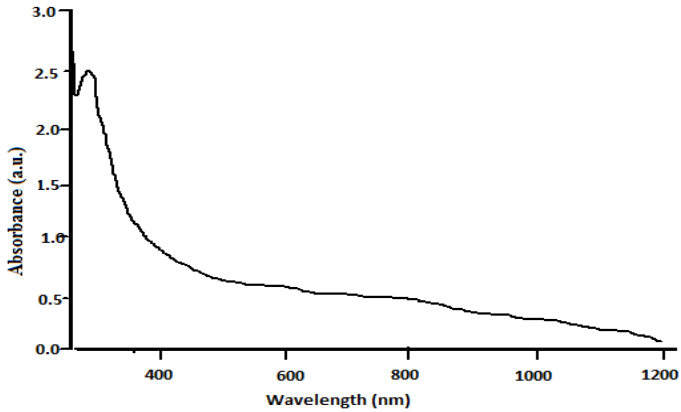


Figure 13. The absorption spectrum of a dispersed solution of silver thiostibitate

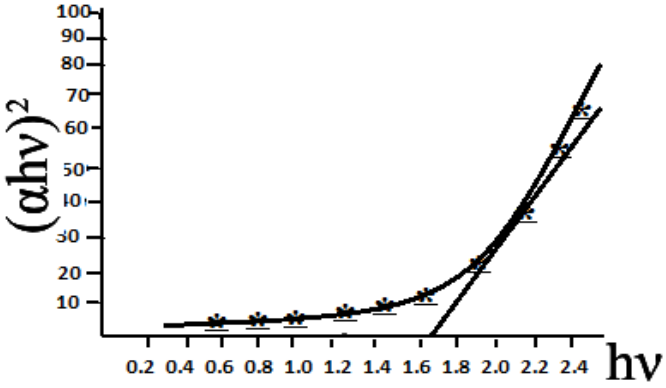


Figure 14. Dependence $(\alpha h\nu)^2$-hν (photon energy) of the Ag_3SbS_4 nanoparticles

Figure 15. Micrographs of Ag_3SbS_4 nanoparticles in a mixture of DMF+TEA.

Investigation of the conditions for the synthesis of thallium(I) thiostibitate by the solvothermal method. 0.25 g of sodium thiostibitate crystalline hydrate ($Na_3SbS_4 \cdot 9H_2O$) is dissolved in a 1:1 mixture of ethyleneglycol+polyethyleneglycol as an organic medium. Thallium nitrate, which is suitable for the reaction, is also dissolved in the same mixture to some extent. Both solutions are transferred to a test beaker and stirred with a magnetic stirrer at a temperature of 70℃ for 30-40 minutes. Then the mixture is collected in a Teflon cuvette, tightly closed, and placed in a microwave oven. The sample is heated in an oven at a temperature of 150℃ for 12 hours. After the process is completed, the precipitate obtained is filtered through a glass filter, washed first with distilled water and then with ethyl alcohol. The purified precipitate is dried in a vacuum at a temperature of 80℃. Preliminary analyses confirmed the presence of all three elements in the sample.

The reaction equation of the process is formulated as follows.

Organic environment.

$$Na_3SbS_4 + 3TlNO_3 \longrightarrow Tl_3SbS_4 + 3NaNO_3 \qquad (13)$$

The diffraction patterns of thallium thiostibitate in water and organic media coincide.

In different solvents The micromorphology of the thallium thiostibitate compound obtained in ethyleneglycol+polyethylene glycol medium, at a temperature of 70℃ and for 12 hours was studied using a HITACHI - TM3000 electron microscope. The results are given in Figure 16.

From the results of SEM analysis, it became clear that the synthesized Tl_3SbS_4 nanoparticles have various shapes (oval and spherical), their diameters are between 250 and 700 nm, and their lengths reach several micrometers.

The morphology of a thallium thiostibitate sample obtained in polyvinylpyrrolidone medium is shown in Figure 17.

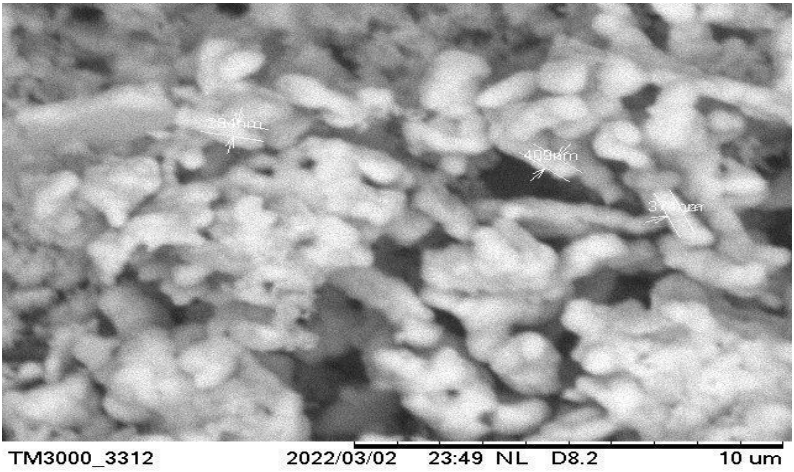


Figure 16. Morphology of Tl_3SbS_4 nanoparticles obtained in ethyleneglycol+polyethyleneglycol medium [9, p. 462]

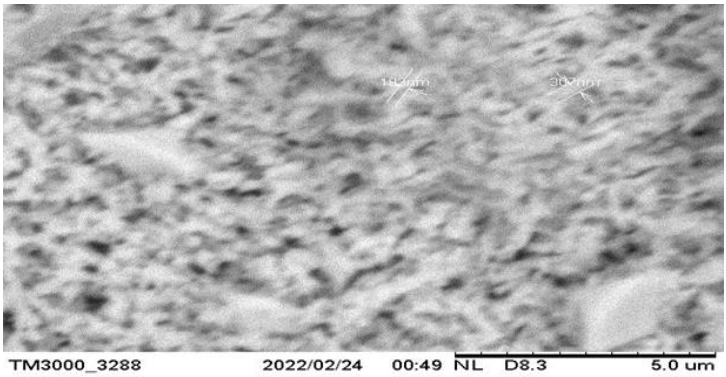


Figure 17. Morphology of Tl_3SbS_4 nanoparticles obtained in polyvinylpyrrolidone medium [9, p. 462]

As can be seen, the particles are in the form of a knotted network, and their sizes vary between 180-350 nm.

In another experiment, dimethylformamide (DMF) with triethanolamine (TEA) was used as a solvent. Thus, a new organic mixture was prepared by mixing one part of triethanolamine with two parts of dimethylformamide (1:2).

Here, most of the particles obtained were wine-like and filled the entire surface. Their sizes vary between 200-560 nm.

Study of the conditions for obtaining antibium (V) thiostibite by the solvothermal method.

The experiments were carried out in the following sequence. In a 50 ml beaker, a certain amount of sodium thiostibite -Na_3SbS_4 is dissolved in ethyleneglycol. In another beaker, a solution of potassium antimonyl tartrate in ethylene glycol is prepared for the reaction. After the solutions are prepared, potassium antimonyl tartrate solution is added to the sodium thiostibite solution under a pH meter in portions and mixed. The reaction equation of the process can be written as follows [8, p. 57].

$$Na_3SbS_4+KSbOC_4H_4O_6+3HCl=SbSbS_4\downarrow+KHC_4H_4O_6+3NaCl+H_2O \quad (14)$$

The mixture was collected in a Teflon cuvette, tightly closed, placed on a heater, and kept at a temperature of 160℃ for 15 hours.

After the process was completed, the solution was filtered through a glass filter. The precipitate was first washed with distilled water, then with ethyl alcohol, and dried at a temperature of 105℃.

Several factors affecting the formation of antimony thiostibitate nanoparticles were studied and optimal conditions were determined. Initially, a thermogravimetric analysis of the sample obtained under optimal conditions was performed. The results of the analysis confirmed the individuality of antimony thiostibitate.

In order to clarify the stoichiometric composition of the antimony thiostibitate compound, elemental analysis of the composition of the obtained compound was performed and micrographs were taken (Fig. 18).

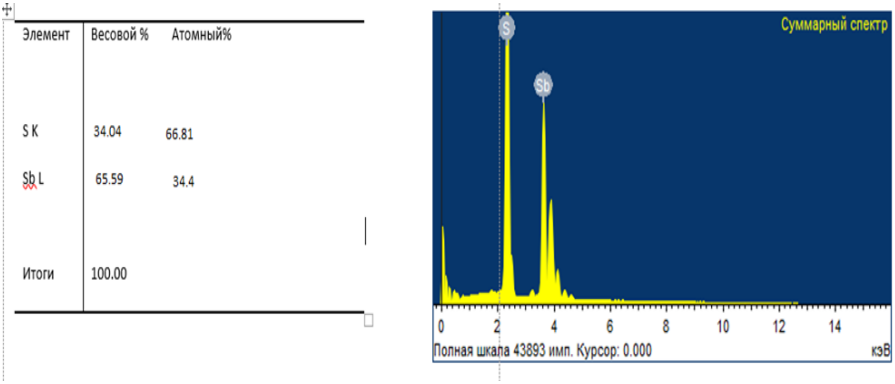


Figure 18. Elemental composition and energy dispersive spectrum of the $SbSbS_4$ nano-compound (8, p. 58]

Based on the results obtained, the mass and atomic ratios of antimony and sulfur in the compound were determined. Based on the results of elemental analysis, it was determined that the simple formula of the compound obtained was $SbSbS_4$.

RESULTS

1. Sodium thiostibitate crystal hydrate ($Na_3SbS_4 \cdot 9H_2O$) was obtained under the determined optimal conditions (temperature 25-85℃, pH=1-4, time 1-3 hours) in the presence of antimony (III) sulfide obtained from Darıdag ore [5].
2. Antimony penta sulfide was synthesized from ethylene glycol and ammonium chloride (pH=2-3) by solvothermal method in the organic medium of 1.5M solution of sodium thiostibitate ($Na_3SbS_4 \cdot 9H_2O$). It was found that at temperature 25-27℃, $SbSbS_4$ (Sb_2S_5) completely precipitates and separates from the solution. The results of elemental analysis show that the composition of the compound corresponds to the stoichiometric composition. According to the results of microstructure analysis, the compound consists of cubic nanoparticles and is an amorphous compound with dimensions of 150-300 nm [8, 16].
3. Thiostibiates of some heavy metals were obtained from sodium thiostibite in an aqueous medium. Copper thioostibite, silver thioostibite, and stibium thioostibite compounds were obtained by the interaction of sodium thioostibite with copper (I) chloride, silver nitrate, and potassium antimony tartrate. The thermodynamic parameters of the obtained compounds were calculated, and XRD and DTA analyses were performed. The melting temperatures of the compounds are in the range of 445-625℃. During the processes, 5 parts of the 8 parts of stibium taken for reactions enter the composition of the compound, and 3 parts pass into the solution [6, 11, 15, 17].
4. The conditions for obtaining sulfosalts containing Cu_3SbS_4, Ag_3SbS_4, Tl_3SbS_4 from the Sb_2S_5-CuCl-H_2O, Sb_2S_5-$AgNO_3$-H_2O, Sb_2S_5-$TlNO_3$-H_2O systems were studied. Based on thermodynamic calculations, the possibility of the corresponding reactions was determined. It was obtained that the normal optimal conditions for obtaining thiostibitates are pH=1-2 and in the 20-70℃ temperature range. The Cu_3SbS_4 compound melts congenerically at 625℃, Tl_3SbS_4 at 480℃, and Ag_3SbS_4 at 440℃ with decomposition. XRD analysis confirms the individuality of the compounds [7,10, 12].

5. It was found that Cu_3SbS_4, Ag_3SbS_4, Tl_3SbS_4 are p-type semiconductors with bandgap of 1.25, 1.70, 1.61 eV, respectively [9, 13].
6. The compounds Cu_3SbS_4, Ag_3SbS_4 and Tl_3SbS_4 were prepared by solvothermal method in ethylene glycol, ethylene glycol+ polyethylene glycol, ethylene diamine, triethanolamine (TEA)+ dimethylformamide (DMF), polyvinylpyrrolidone, Na_3SbS_4 and ammonium chloride. Thermogravimetric, XRD, and chemical analysis of the compounds obtained under the conditions of factors affecting the preparation of the compounds (amount of organic solvents, pH of the medium, temperature, concentration of components, and time) were carried out, their morphology was studied and it was determined that they are in the form of nanoparticles [9, 13, 16].
7. Based on the value of the width of the forbidden zone, the compounds Cu_3SbS_4, Ag_3SbS_4, and Tl_3SbS_4 have been recommended for use in energy converters (solar cells), and the compound $SbSbS_4$ for the production of mineral lubricants [10, 11, 13, 16,].

The main results of the dissertation work were published in the following works:

1. B.Z. Rzayev, S.H. Əliyeva. Darıdağ sürmə filizindən sürmə (III) sulfidin və talliumun tiantimoniatın alınma şəraitinin tədqiqi // AMEA Naxçıvan Bölməsi Xəbərlər, Naxçıvan "Tusi" 2019 № 4 s. 16-20
2. S.H.Kərimova, Q.M. Hüseynov. Mis(I) tetratioantimoniat nazik təbəqələrin alınması və xassələrinin tədqiqi // Müasir kimyanın aktual problemləri Beynəlxalq elmi konfrans,-Bakı: SOCAR, 2-4 oktyabr,-2019,-s.472
3. S.H.Əliyeva, Hüseynov Q.M. Hidrokimyəvi metodla Tl_3SbS_4 birləşməsinin alınması // Seconda İnternational Scientific Conference of Young Scientists and Specialist SOCAR, 03-06 Mart 2020, p.315-317.
4. Q.M. Hüseynov, S.H. Əliyeva Hidrotermal şəraitdə Tl^+-

$Sb^{3+}(Sb^{5+})$-S^{2-}-H_2O sistemlərindən üçlü sulfidlərin alınması // AMEA Naxçıvan Bölməsi Xəbərlər, Naxçıvan "Tusi" 2020 № 4 cild 16 s. 30-36
5. S.H. Əliyeva Natrium tiostibıatın alınması şəraitinin araşdırılması // AMEA Naxçıvan Bölməsi Xəbərlər, Naxçıvan "Tusi"2021 № 4 cild 17 s. 51-55
6. S.H. Əliyeva Na_3SbS_4-$AgNO_3$-H_2O sistemində gümüş tiostibiatın alınma şəraitinin araşdırılması / AMEA Naxçıvan Bölməsi Xəbərlər, Naxçıvan "Tusi" 2022 № 2 cild 18 s. 59-67
7. S.H. Əliyeva, A.B. Rzayeva, Sb_2S_5-$TlNO_3$-H_2O sistemində tallium tiostibiatın alınması şəraitinin araşdırılması // AMEA Naxçıvan Bölməsi Xəbərlər, Naxçıvan "Tusi" 2022 s. 39-46
8. Ə.M.Qarayev, S.H. Əliyeva. Sürmə tiostibiatın alınması şəraitinin araşdırılması // Təbiət və Elm beynəlxalq elmi jurnal 2022 № 6 cild 4s. 55-59
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13. S.H. Aliyeva, A. B. Rzayeva. Synthesıs of copper thıostıbıate nano compound by solvothermal method // Journal of Chemistry and Technologies 2024 № 2 Vol 32 p. 304-311
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16. S.H. Aliyeva. Investigation of the conditions for obtaining antimony (V) sulphide by solvothermal method / Materials of the 47th International Scientific and Practical Conference Krakow (Poland) August 7, 2024, p. 226-229.
17. S.H.Əliyeva, Q.M.Hüseynov. Na_3SbS_4-CuCl-H_2O sistemindən alınan birləşmələrin sintezi // Elm və Təhsilin əsasları IX Beynəlxalq elmi konfrans 09.08.2024 s. 114-117

The defense will be held on 23 January 2025 at $10^{\underline{00}}$ at the meeting of the Dissertation Council ED 1.15 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating in the Institute of Catalysis and Inorganic Chemistry named after acad. M.Nagiyev.

Address: H.Javid ave.,113, AZ-1143, Baku, Azerbaijan
E-mail: kqki@kqki.science.az

The dissertation is accessible at the acad.M.Naghiyev Institute of Catalysis and Inorganic Chemistry library.

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Abstract was sent to the required addresses on 23 December 2024

Signed for print: 05.12.2024
Paper format: 60x84$^{1/16}$
Volume: 37 050
Number of hard copies: 20