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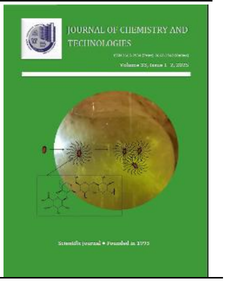

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INVESTIGATION OF CONDITIONS FOR OBTAINING AG_3SBS_4 NANOPARTICLES IN VARIOUS ORGANIC SOLVENTS

Sevda H. Aliyeva*, Aliye B. Rzayeva, Gorkhmaz M. Huseynov, Shamil M. Mahmudov,
Bahruz G. Mammadov
Nakhchivan State University, Dilgam Pishavari, Nakhchivan, AZ7012, Azerbaijan

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Abstract

Ag_3SbS_4-nanocrystals were synthesized by solvothermal method in various member solvents (ethylene glycol+polyethylene glycol) and (dimethylformamide+triethenolamine). Optimum conditions for obtaining nanoparticles were determined (molar ratios of the amount of components, volume ratio of the solvent, temperature, time, etc.). The crystal structure, morphology, nano-size and chemical composition of the obtained silver thiostibiate nanostructure were studied using thermogravimetric (TG), X-ray powder diffractometer (XRD), energy dispersion spectroscopy (eds) and transmission electron microscopy (TEM). Using EDX and chemical analysis, the composition was found to correspond to the formula Ag_3SbS_4. The results of the TEM analysis showed that the synthesized Ag_3SbS_4 nanowires have diameters ranging from 150 to 200 nm, while their lengths can reach several micrometers. The dispersion solution of Ag_3SbS_4 nanoparticles was prepared in n-heptane, and the forbidden band width was determined from the absorption spectrum of the solution.

Keywords: nanocrystals; ethylene glycol + polyethylene glycol; dimethylformamide + triethanolamine; n-heptane.

ДОСЛІДЖЕННЯ УМОВ ОТРИМАННЯ НАНОЧАСТИНОК Ag_3SbS_4 У РІЗНИХ ОРГАНІЧНИХ РОЗЧИННИКАХ

Севда Г. Алієва, Алія Б. Рзаєва, Горхмаз М. Гусейнов, Шаміль М. Махмудов,
Бахруз Г. Мамедов
Нахічеванський державний університет, Ділгам Пішаварі, Нахічевань, AZ7012, Азербайджан

Анотація

Нанокристали Ag_3SbS_4 синтезовано сольвотермічним методом у розчинниках з різним складом компонентів (етиленгліколь+поліетиленгліколь) та (диметилформамід+тритеноламін). Визначені оптимальні умови одержання наночастинок (мольні співвідношення кількостей компонентів, об'ємні співвідношення розчинників, температура, час тощо). Кристалічну структуру, морфологію, нанорозміри та хімічний склад отриманої наноструктури тіостибіату срібла вивчали за допомогою термогравіметричного аналізу (ТГ), рентгенівської порошкової дифрактометрії (РФА), енергодисперсійної спектроскопії (ЕДС) та трансмісійної електронної мікроскопії (ТЕМ). За допомогою EDX та хімічного аналізу було встановлено, що склад відповідає формулі Ag_3SbS_4. Результати ТЕМ-аналізу показали, що синтезовані нанодроти Ag_3SbS_4 мають діаметр від 150 до 200 нм, тоді як їх довжина може досягати декількох мікрометрів. Дисперсійний розчин наночастинок Ag_3SbS_4 готували в н-гептані, а ширину забороненої зони визначали зі спектра поглинання розчину.

Ключові слова: нанокристали; етиленгліколь + поліетиленгліколь; диметилформамід + триетаноламін; н-гептан.

**Corresponding author: e-mail:* sevda.nihad2019@gmail.com

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Introduction

The name “ruby silvers” was used by miners to indicate the reddish minerals that were often found in silver deposits. In the first half of the 19th century it was recognised that this material could be traced back to four different species – very similar to each other, not only in appearance, but also in the chemical composition, as they consisted of “sulfoarsenite” or “sulfoantimonite” of silver (Ag_3AsS_3–Ag_3SbS_3) – in two polymorphic series, the trigonal one, formed by proustite and pyrargyrite, and the monoclinic one, consisting of xanthoconite and pyrostilpnite [1]. The system Ag-Sb-S was studied between 600 °C and 200 °C in evacuated silica glass tubes. Results from lower temperature runs require shifts in the stable tie-line configuration found by Barstad at 400 °C. It is proposed that the configuration changes near 300 °C, and that at 200 °C the equilibrium assemblages correspond to those usually reported for minerals in ores. Most of the minerals of the system were synthesized [2].

Recently, researchers have begun to pay attention to chalcogenide semiconductor systems such as $A^IB^VC^{VI}$. From this class of compounds, thio compounds formed by antimony with heavy metals (e.g. $AgSbS_2$, Ag_3SbS_3) are recognized as important functional materials of modern technology. Nanocomposites obtained from the Ag-Sb-S system are widely used in the production of valuable semiconductors, photoelectric and ferroelectric materials, electro-optic materials, solid electrolytes, electrochemical sensors, electrochemical displays, etc. At the same time, the use of silver-based Triple sulfide (SC) semiconductor nanoparticles for the development of renewable energy sources is noteworthy. Our research opens up another prospect for pursuing high performance $AgSbS_2$ thin film solar cells by adopting a solution processing method and planar heterojunction device structure. [3]

Using visible light beams as a photocatalyst, the conditions for the chemical synthesis of Ag_3SbS_3 in the presence of metal-thiocarbamide complexes in an ethylene glycol medium have been studied. The individuality of Ag_3SbS_3 was confirmed by X-ray phase analysis. From SEM images, it was determined that its morphology does not exist. From UV spectroscopy measurements, the width of its forbidden band for Ag_3SbS_3 was determined to be 1.77 eV. Under visible light rays by Ag_3SbS_3 it exhibited rapid dehydration against methylene blue, methyl orange, malachite green, and rhodamine 6G dye solutions. All these processes were associated with mesopores (3 nm) resulting from the synthesis of Ag_3SbS_3 with a high surface area (3.81 m6.39 m^2/g), its catalytic activity [4]. A large number of silver-based triple sulfide semiconductors (SC) have been considered for the sustainable development of renewable energy sources. As a result of thermal decomposition of silver and antimony-based dithiocarbamate (~N-CS_2-M) complexes, two important classes of semiconductor nanocrystals (NCs) Ag_3SbS_3 (SAS) were synthesized (hexagonal and monoclinic). It’s interesting that these two systems exhibit two different semiconductor (SC) properties and band gaps; hexagonal SAS has p-type and ~1.65 eV, while monoclinic SAS has n-type (~2.1 eV). The physicochemical stability and reusability of both materials were supported by electrochemical chronoamperometric measurements extended for 50 hours and powder XRD and TEM analyzes after electrocatalysis [5]. A new biomolecular method was developed for obtaining pyrargyrite (Ag_3SbS_3) nanowires from the interaction of L-cysteine, silver nitrate and antimony(III) chloride in an ethylene glycol medium at a temperature of 200 °C for 15 hours. Here, L-cysteine was used as a source of sulfide and a complexing reagent. The crystal structure, morphology, nanoscale size, and chemical composition of the prepared products were studied using X-ray powder diffraction (XRD), energy dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). From the results of the analysis, it was determined that the synthesized Ag_3SbS_3 nanowires have diameters from 150 to 200 nm, and lengths up to several micrometers. Experiments have established that the duration of the process played an important role in the formation of Ag_3SbS_3 nanocrystals [6]. Thin layers of Ag_3SbS_3 were made using the method of evaporation in vacuum at temperatures above Sb_2S_3 and Ag nanoparticles. The obtained thin layers were annealed in the air atmosphere at 250 °C and 300 °C and characterized using XRD, SEM, AFM, UV, FTIR and other methods. Thin layers showed softening (amorphous) at temperatures below 250 °C, whereas the monoclinic structure of Ag_3SbS_3 should have shown softening at temperatures above 250 °C. Optical-structural and electrical analysis showed that thin layers of Ag_3SbS_3 have an important property as potential absorbers for photovoltaic applications [7]. Nanoparticles of Ag_3SbS_3 from ternary metal chalcogenides were synthesized by hydrothermal method. In the next process, thin layers of Ag_3SbS_3 were obtained after deposition of Ag_3SbS_3 nanoparticles. We present a ternary semiconductor nanoparticle sensitizer – $AgSbS_2$ –for solar cells. $AgSbS_2$ nanoparticles were grown using a two-stage successive ionic layer adsorption and reaction process. First, Ag_2S nanoparticles were grown on the surface of a nanoporous TiO_2 electrode. Secondly, a Sb–S film was coated on top of the Ag_2SThe best Ag_3SbS_3 nanoparticles were obtained by hydrothermal reaction at a temperature of 140 °C and a period of 12 hours. The formation of thin layers of Ag_3SbS_3 is sensitive to softening temperatures, and its best thin layers were synthesized at 440 °C. XRD determined that the Ag_3SbS_3 sample was single-phase. The prepared Ag_3SbS_3 nanoparticles have a smooth, uniform surface with an average size of ~200 nm. It has been found that the width of the forbidden zone is 1.8 eV and the absorption coefficient at λ=400 nm is 2.1×10^5 cm^{-1}. The large coefficient of optical absorption indicates that thin layers of Ag_3SbS_3 can be a potential solar converting material. Compared to the laser technique currently used, this method is simpler, cheaper and capable of producing high-quality Ag_3SbS_3 thin layers [8; 9]. The thermal evaporation and post-sedimentation heating process were used to make the photoconductive Ag-Sb-S thin layer. First, to obtain Ag_2S/Sb_2S_3/ substrate samples, both Sb_2S_3, and Ag_2S compounds are successively evaporated. Secondly, Ag-Sb-S thin films were converted into a bilayer structure through post-annealing operations. Optical absorption studied suggested that the $AgSbS_2$ film prepared at 350 °C exhibited a direct bandgap of 1.61 eV. As a result, the coexistence of monoclinic $AgSbS_2$ and hexagonal Ag_3SbS_3 phases was determined [10; 11]. Doehlert matrix was used to correlate between the effect of several factors and to predict the optimal condition of thickness (e ¼ 4 mm). XRD and SEM techniques were used to study the structural, microstructural and morphological properties of the obtained film. XRD data confirm the formation of the desired phase as well as their purity. SEM analysis reveals that the obtained film has a morphology of truncated plate-shaped grains. The optical band gap (Eg) of this film was determined from transmittance and reflectance data and it was found to be equal to 1.65 eV. DFT calculation was applied to investigate the electronic structure of the material and to confirm the experimental optical results. $AgSbS_2$ shows good photocatalytic activity with a degradation efficiency of 80% for three hours [12]. we identified the coexistence of cubic and monoclinic $AgSbS_2$ and monoclinic and hexagonal Ag_3SbS_3 phases. In addition, the evolution from metastable to stable phases of $AgSbS_2$ and Ag_3SbS_3 is presented [13], In this study, the impact of precursor stacking sequence and sulfurization duration on the growth and properties of Ag_3SbS_3 films was investigated. Initially, Ag_3SbS_3 films produced by depositing Sb/Ag and Ag/Sb/Ag metal stacks and then sulfurizing at 300 °C were crystallized in rhombohedral structure with a preferred orientation (113). The film produced from the Sb/Ag stack had a uniform and large-grained morphology up to a thickness of 1150 nm, and a direct bandgap of 1.65 eV; whereas the film prepared with the Ag/Sb/Ag stack exhibited nonuniform grain morphology with decreased film thickness and increased bandgap energy (1.70 eV). Secondly, Ag_3SbS_3 films produced from the Sb/Ag stack by increasing sulfurization duration from 10 to 90 min increases the crystallite size from 26 to 27 nm, enhances the grain compactness and uniformity, varies the bandgap in the range of 1.65–1.69 eV, and electrical resistivity. All of this enabled us to conclude that Ag_3SbS_3 possesses the physicochemical characteristics to make it an attractive option in the disciplines of supercapacity as well as photovoltaic. For optimal manufacturing, Ag_3SbS_3 thin films were electrodeposited on Fluorine-Tin Oxide (FTO) and then sulfurized at different temperatures. Ag3SbS3 thin films formed by annealing hydrothermally synthesized Ag_3SbS_3 nanoparticles [14–16]. In this work, we investigate Ag_3SbS_4 by first-principles means, since the optical properties of this compound can be expected to improve. The results indeed demonstrate that enargite Ag_3SbS_4 is a direct-gap semiconductor with a band gap of 1.38 eV, thus optimal for single-junction solar cells. Furthermore, its carrier effective masses, optical coefficients and spectroscopic limited maximum efficiency are comparable to well-established PV compounds. The compound exhibits also thermodynamical and dynamical stability Thermodynamic functions of $AgSbS_2$ and Ag_3SbS_3 have been determined. Accurate thermodynamic properties of both phases including data in new temperature ranges have been obtained [17; 18].

During the analysis of literature materials, There are no data on obtaining nanoparticles and microparticles of silver thiostibiate – $Ag_3SbS_{4.}$ Therefore, the above paper presents the results of studies related to the preparation of nano- and microparticles of combined silver thiostibiate as a result of the interaction of sodium thiostibiate and $AgNO_3$ in organic medium.

Experimental part

a). The experiments were carried out in the following order: 0.25 g sodium thiostibiate crystallhydrate (Na_3SbS_4. $9H_2O$) is dissolved in a mixture of ethylene glycol + polyethylene glycol as an organic medium taken in a ratio of 1 : 1. The silver nitrate corresponding to the reaction is also dissolved in the mixture to a certain extent. Both solutions are mixed in a test vessel. The mixture is mixed with a magnetic mixer at a temperature of 616 °C and a duration of 30–40 minutes. Then, the mixture is placed in a teflon cuvette, sealed tightly, and placed in a microwave oven. The sample was heated in an oven at 696 °C for 18 hours. After the process was completed, the obtained precipitate was filtered, first washed with distilled water, and then with ethyl alcohol. The cleaned precipitate was dried in vacuum at a temperature of 626 °C. Preliminary analyses confirmed the presence of all three elements in the sample.

The reaction equation of the process is formulated as follows.

$$Na_3SbS_4 + 3AgNO_3 \xrightarrow{\text{Organic env.}} Ag_3SbS_4 + 3NaNO_3$$

In the experiments, we used weights corresponding to the mole amount of the primary components. Therefore, we found it appropriate to show the experimental weights in Table 1. We converted the substances taken in the table to moles and made the table again.

The dependence of the mass of silver thiostibitite formed in organic medium on the amount of silver nitrate was studied and the results are given in Table 1.

Table 1

Dependence of the mass of the obtained Ag_3SbS_4 on the amount of silver nitrate

Na_3SbS_4, mol	$AgNO_3$, mol	Ag_3SbS_4 q	
		pract.	theoretic.
0.001	0.0015	0.2797	0.2870
0.001	0.0020	0.3818	0.3827
0.001	0.0025	0.4778	0.4783
0.001	0.0030	0.5739	0.5740
0.001	0.0040	0.5739	0.5740

As can be seen from the table, the compound is formed in the system regardless of the change in the amount of silver nitrate. In fact, increasing the amount of silver nitrate does not lead to an increase in the mass of the sample.

The results of the preliminary chemical analysis of the composition of the sample obtained in the ethylene glycol+polyethylene glycol medium are presented in Table 2. After taking a certain amount from the silver thiostibiate sample, a small amount of nitric acid solution was added to it and heated until the sample dissolved and the solution evaporated completely. After completing the process, the dry residue was dissolved in distilled water and filtered through a glass filter. The insoluble fraction (Sb_2O_5) was washed clean, dried and weighed. From here the mass of the antimony is determined. The determination of the amount of silver in the filtrate was carried out by the faience method. The sulfur content in the sample was determined by the barium nitrate titration method.

Table 2

Chemical analysis of silver thiostibiate compound

The amount of sample, q	The amount of items, q					
	Ag		Sb		S	
	Theoretical	Practical	Theoretical	Practical	Theoretical	Practical
0.287	0.1621	0.1584	0.0608	0.0573	0.064	0.0609

According to the results of the chemical analysis of the sample, it was confirmed that the composition of the compound corresponds to silver thiostibiate.

The stoichiometric composition of the compound was determined by TGA (NETZSCH STA 449F3) analysis. (Figure 1).

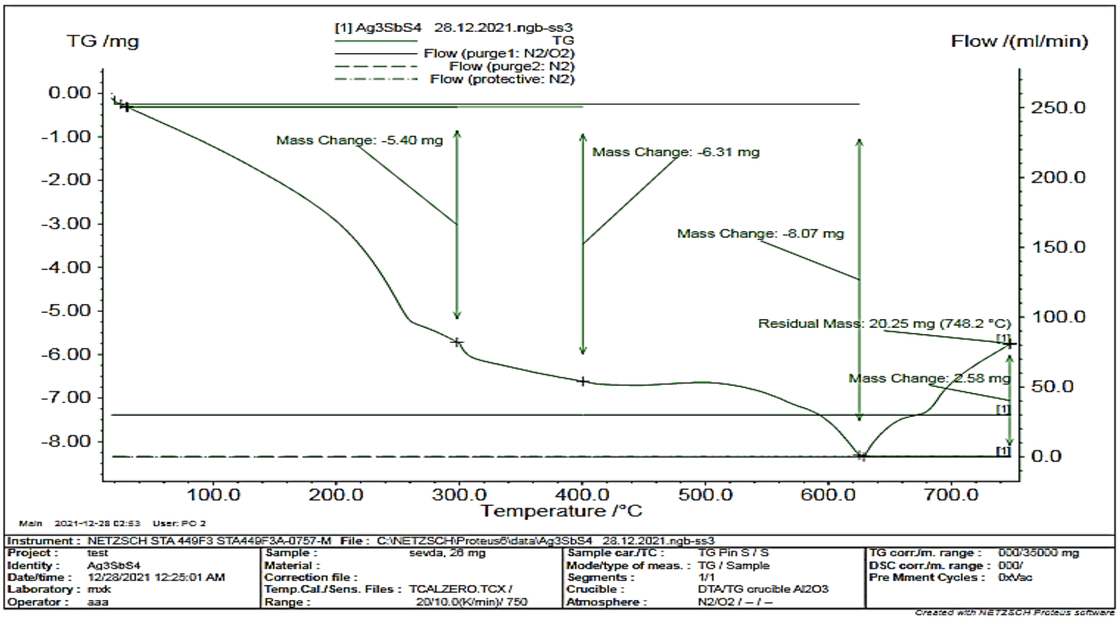


Fig. 1. Derivatogram of silver thiostibiate compound

As can be seen from Fig.1, the 26 mg sample taken for analysis was heated to a temperature of 750 °C. Theoretically, it is known that the 26 mg sample contains 5,798 mg of sulfur, 5.52 mg of antimony and 14.67 mg of silver. The mass loss during the analysis was 8.07 mg at the temperature range of 200–640 °C. 5.8 mg of sulfur is lost, so (5.8–5.8 = 0. S) 3.30 mg of 5.52 mg of stibium is lost, leaving 2.2 mg. (5.52–3.3 = 2.2 mg Sb). The reason is that during the initial oxidation of antimony, a certain amount of antimony (III) oxide is obtained and sublimated. However, as the temperature increases, antimony (III) oxide turns into antimony(V) oxide. This is a stable oxide. The increase in mass during the increase in temperature above 640 °C was due to the oxidation of antimony and silver. Thus, when 14.67 mg of silver in a 26 mg sample is oxidized, 15.64 mg of Ag_2O is formed. Antimony is 5.52 mg per sample. After sublimation of 2.2 mg of it, oxidation of the remainder (3.32 mg) gives 4.57 mg of oxide. The total of these oxides was 15.64 + 4.57 = 20.21 mg. It can be seen in the thermogram that the residue was 20.25 mg, which was the same as the experimental value. Based on these results, it was confirmed that the simple formula of the compound is silver thiostibiat

The structural structure and individuality of silver thiostibiate compound synthesized in ethylene glycol+polyethylene glycol medium was determined by X-ray phase analysis and Figure 2. The X-ray diffraction measurements were performed using the X-ray analyser 2d Phaser “Bruker” [19]

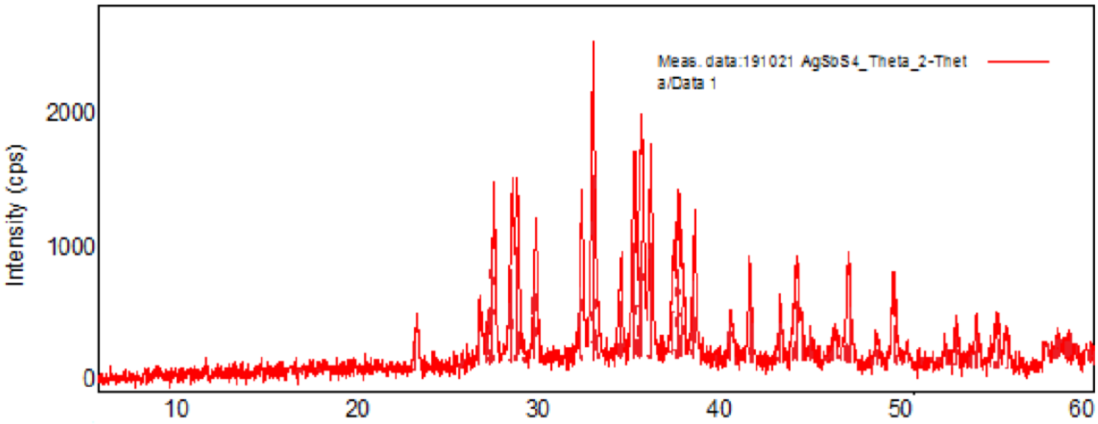


Fig. 2. Diffractogram of Ag_3SbS_4 compound obtained in organic environment

As a result of the analysis, it was found that silver thiostibiate was the main component of the compound obtained in the organic environment These compounds are mainly in the amorphous state. The micromorphology of the silver thiostibiate compound obtained at 616° C was studied in a Hitachi-TM3000 brand electron microscope (Figure 3).

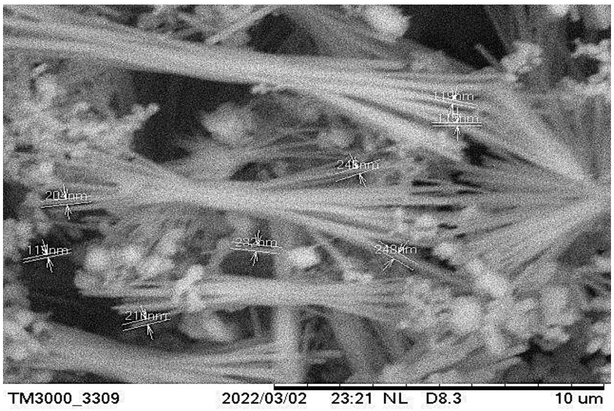
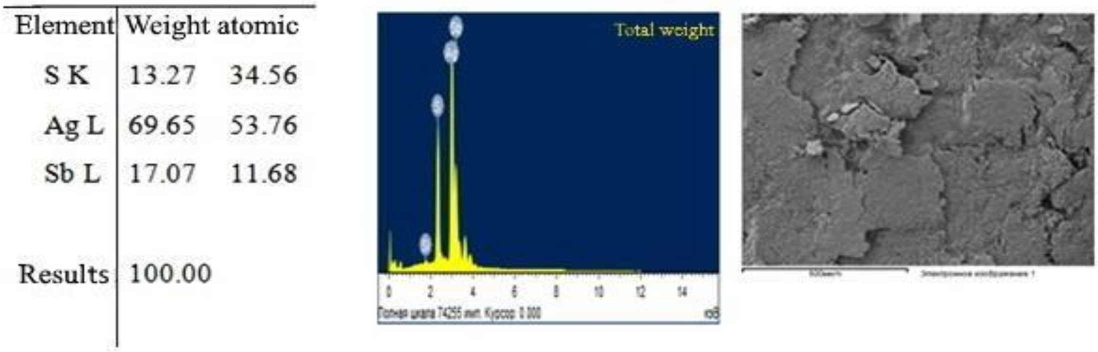


Fig. 3. Microphotography of silver thiostibiate compound

From TEM analysis, it was clear that the diameter of the synthesized Ag_3SbS_4 nanotubes ranged from 150 to 300 nm, while their length reaches several micrometers.

Figure 4 presents the results of element analysis, energy-dispersed spectrum and electron images of silver thiostibiate compound obtained in ethylene glycol+polyethylene glycol environment. (JSM-6610LV SEM – Oxford Instrument)



Element	Weight	atomic
S K	13.27	34.56
Ag L	69.65	53.76
Sb L	17.07	11.68
Results	100.00	

Fig. 4. Element composition and energy-dispersed spectrum of the Ag_3SbS_4 compound

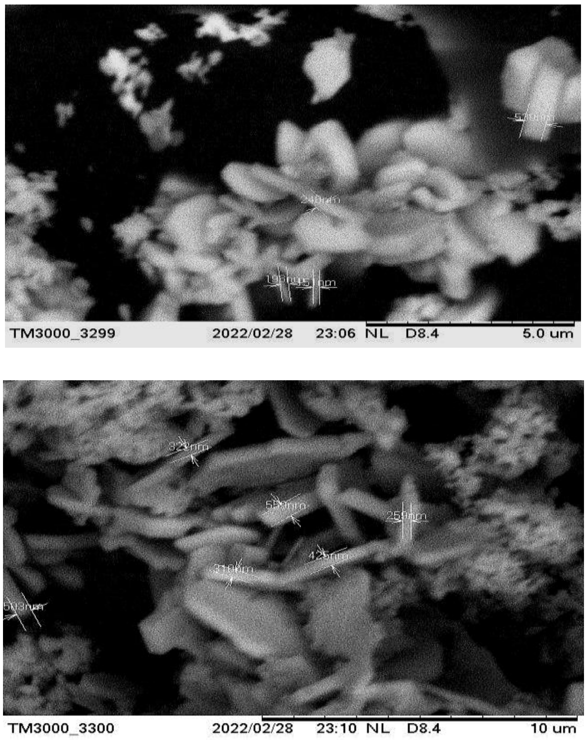


Fig. 5. Electronic images of silver thiostibiate compound

According to the results of the elemental analysis, it was concluded that the simple formula of the compound obtained according to the values of the mass and atomic ratios of the elements in the compound - silver, antimony and sulfur – corresponds to silver thiostibiat.

A solution of a certain amount of silver thiostibiate dispersed in 20 ml of n-heptane was prepared and the optical properties of this solution were studied. The absorption spectrum of the solution in 1 cm cuvettes was recorded using a U-5100 Hitachi ultraviolet spectrophotometer, and the optical absorption curve was plotted with the established dependencies.

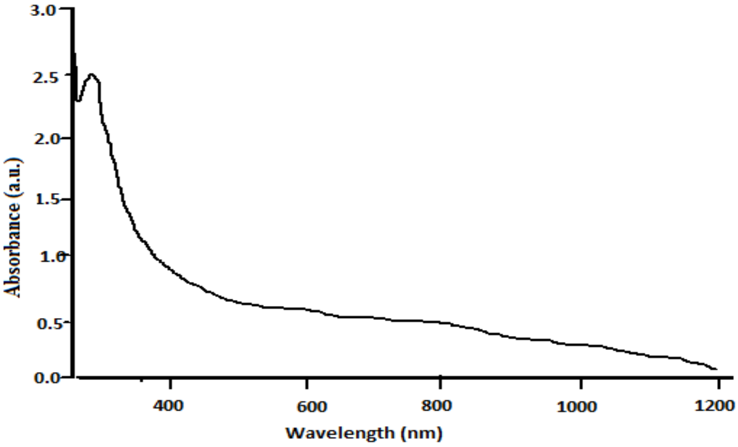


Fig. 6. Absorption spectrum of dispersed solution of silver thiostibiate

It is known that the width of the forbidden zone of the solutions and thin films of semiconductor compounds can be calculated using the Tauc formula:

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\nu - E_g).$$

According to the formula, the values of $(\alpha h\nu)^2$ and hν, and based on the obtained values, the dependence curve of $(\alpha h\nu)^2$ on hν was plotted, determining the value of the forbidden zone width of the compound.

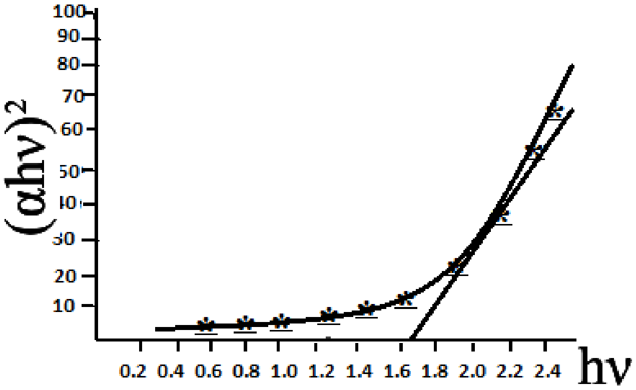


Fig. 7. Dependence of nanoparticles of Ag$_3$SbS$_4$- compound on $(\alpha h\nu)^2$ - hν (photon energy)

As can be seen from the graph, the width of the forbidden zone of Ag$_3$SbS$_4$- nano compound synthesized by the solvothermal method was equal to Eg = 1.70 eV.

b). The experiments were carried out under the same conditions but in a mixture of other organic solvents. Dimethylfarmamide (DMF) and triethanolamine (TEA) were used as organic solvent. Thus, one part of triethanolamine was mixed with two parts of dimethylformamide (1 : 2) to prepare a new organic mixture. Since triethanolamine is a highly viscous solution, it was diluted with dimethylformamide. 0.25 g sodium thiostibiate crystallhydrate (Na$_3$SbS$_4$. 9H$_2$O) is dissolved in 25 ml of the mixture [20]. After the silver nitrate suitable for the reaction is dissolved in that mixture to a certain extent, both solutions are collected in the experimental vessel. The mixture is mixed with a magnetic mixer at a temperature of 616 °C and a duration of 30–40 minutes. The reagents are then collected in a Teflon cuvette, capped, and placed in a microwave oven. The sample was kept in the oven at a temperature of 696 °C for 18 hours. After the completion of the process, the resulting sediment was filtered through a filter, washed first with distilled water, and then with ethyl alcohol. The morphology of the silver thiostibiate compound obtained at a temperature of 616 °C was studied under a Hitachi-TM3000 brand electron microscope (Figure 7).

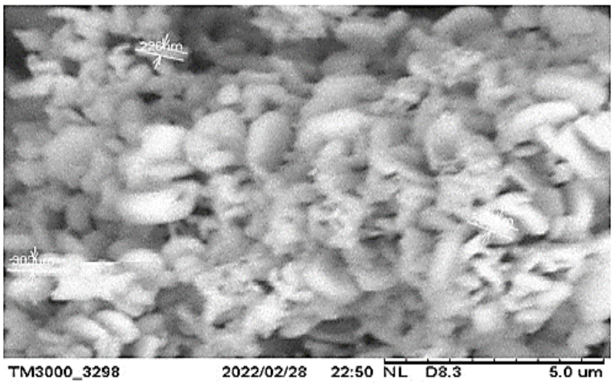


Fig. 8. Micrographs of Ag_3SbS_4 - nanoparticles in DMF+TEA mixture

As can be seen from the figures, when solvents change, the shape of the particles also changes. The particles are arranged in hexagonal layers. The thickness of the layers was 250–500 nm. The size of the tiles of the hexagon was in the range of several microns. It was established by experiments that no other changes in the properties of the compound occurred. The forms of nanoparticles have changed.

Conclusion

Ag_3SbS_4 nanocrystals were synthesized by solvothermal method in the presence of $AgNO_3$ and Na_3SbS_4 in ethylene glycol + polyethylene glycol environment. Optimum conditions for obtaining nanoparticles have been determined (molar ratios of the amount of components, volume ratio of the solvent, temperature, etc.). It was determined by thermogravimetric, EDX and chemical analysis that the nanocomposition of silver thiostibiate corresponds to the Ag_3SbS_4 formula. The structural structure (individuality) of the sample was confirmed by XRD. The morphology of the sample was studied with an electron microscope and pictures of nanoparticles were taken. A dispersed solution of Ag_3SbS_4 nanoparticles in n-heptane was prepared, and the width of the forbidden zone was found based on the absorption spectrum of the solution. The same experiments were carried out in dimethylformamide (DMF) with triethanolamine (TEA) as an organic solvent. It was found that the properties of the compound were the same, but the forms of nanoparticles were different.

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