Journal of Chemistry and Technologies, 2024, *32*(2), 304-311

Journal of Chemistry and Technologies

pISSN 2663-2934 (Print), ISSN 2663-2942 (Online).

journal homepage: http://chemistry.dnu.dp.ua
editorial e-mail: chem.dnu@gmail.com

UDC 542+544.2

SYNTHESIS OF COPPER THIOSTIBIATE NANO COMPOUND BY SOLVOTHERMAL METHOD

Sevda H.Aliyeva*, Aliya B. Rzayeva
Institute of Natural Resources under the Ministry of Science and Education of Azerbaijan, Nakhchivan State University, AZ7012
Received 2024; accepted 2024; available online 25 July 2024

Abstract

Nanosized particles produced have many uses. There are different methods of obtaining these particles. Methods using biological systems as environmentally friendly reducing agents are of great interest. The study reports a simple and readily available synthesis of copper-antimony sulfide nanocrystals. The samples were synthesized by the solvothermal method using several substances (copper, antimony, and elemental sulfur). During the experiments, potassium antimonyl tartrate was used as an antimony material, and sulfur ethylenediamine solution was used as sulfide material. The synthesis of Cu_3SbS_4 nanoparticles was carried out by adjusting the molar ratio of sulfur to copper and controlling the volume ratios of the solvent and organic medium (ethylene glycol + polyethylene glycol). The process was carried out at a temperature of 383–393 K for 12 hours and copper-thiostibiate nanoparticles were synthesized with a yield of 85 %. The properties of the obtained nanoparticles were studied by physical and chemical analysis methods – TGA, RFA, TEM, EDS.

Keywords: solvothermal method; copper thiostibiate; nanocrystals; micromorphology.

СИНТЕЗ НАНОСПОЛУК МІДІ З ТІОСТИБІАТАМИ СОЛЬВОТЕРМІЧНИМ МЕТОДОМ

Севда Г.Алієва, Алія Б. Рзаєва
Інститут природних ресурсів при Міністерстві науки і освіти Азербайджану, Нахічеванський державний університет,

Анотація

У науковому дослідженні описано простий і легкодоступний синтез нанокристалів сульфіду купрума-стібія. Зразки були синтезовані сольвотермічним методом з використанням ряду речовин (мідь, сурма та елементарна сірка). В експериментах використовували антимонілтартрат калію як джерело сурми, а розчин сульфату етилендіаміну – як вихідна речовина сульфіду. Синтез наночастинок Cu_3SbS_4 здійснювали шляхом регулювання мольного співвідношення сірки до міді та контролю об'ємних співвідношень розчинника і органічного середовища (етиленгліколь + поліетиленгліколь). Процес проводили за температур 383–393 К протягом 12 годин і синтезували наночастинки тіостибіату купруму з виходом 85 %. Властивості отриманих наночастинок досліджували методами фізико-хімічного аналізу – ТГА, РФА, ТЕМ, EDS.

Ключові слова: сольвотермічний метод; тіостибіат міді; нанокристали; мікроморфологія; мікроморфологія.

**Corresponding author: e-mail: aysel.nuriyeva5@gmail.com*

doi: 10.15421/jchemtech.v32i2.299093

Journal of Chemistry and Technologies, 2024, *32*(2), 304-311

Introduction

Currently, the synthesis and properties of compounds formed by chalcogenides (S, Se and Te) with metals and pnictides (P, As, Sb and Bi) are intensively studied. These compounds have semiconducting and luminescent properties. Also, these compounds are functional materials with wide perspectives as superconductors, magnets, topological insulators, catalysts, etc. Of these, copper-based chalcogenide compounds ($CuSbS_2$, Cu_3SbS_3, $Cu_{12}Sb_4S_{13}$ and Cu_3SbS_4) and their nanoparticles and thin films are important components of solar converter elements and have thermoelectric and photovoltaic properties (6,7,9,12,18). Since copper antimony sulfide (CAS) materials are promising, the preparation and properties of their nanoparticles and thin films have been of recent interest.

The compounds $CuSbS_2$, Cu_3SbS_3, $Cu_{12}Sb_4S_{13}$ and Cu_3SbS_4 are known in the scientific literature. The names of these compounds are given as thio compounds or polysulfides. We have listed it as copper thiostibiate in all our research results. The full name of the Cu_3SbS_4 compound is copper(I) tetrathiostibiate. We believe that we did not make a mistake in naming the substances as sulfur, which plays the role of a ligand, is "thio". The formula of antimony trioxide is more commonly used in the literature as H_3SbO_4.

In this work, the preparation of copper antimony sulfide nanocrystals using the solvothermal method and the study of their properties are given. Phase-pure and quasi-monodisperse Cu_3SbS_4 nanocrystals were synthesized by adjusting the molar ratio of sulfur to copper (S:Cu). The morphology and chemical composition of nanocrystals were characterized (3). In this study, the conditions for simultaneous production of $Cu_{12}Sb_4S_{13}$ and Cu_3SbS_4 thin films by chemical deposition were given (5). Ternary compounds were obtained during the chalcogenation process by spraying metallic substances into the sulfur atmosphere. During sulfur evaporation, the $Cu_{12}Sb_4S_{13}$ phase dominates at a temperature of 140 °C, and a Cu_3SbS_4 phase is formed at a temperature of 180 °C. The composition was analyzed by energy dispersive spectroscopy. Structure analysis and phases were determined by RFA. The optical properties of the obtained compound were studied in thin films deposited directly on a glass substrate. A band gap of 1.47 eV and 0.89 eV was found for $Cu_{12}Sb_4S_{13}$ and Cu_3SbS_4, respectively (5). In this experiment, the synthesis method of monodisperse copper antimony sulfide (CAS) nanocrystals is reported for the first time. This material represents a new class of both I-V-VI semiconductor nanocrystals and all antimony-based nanocrystals. CAS nanocrystals are suitable for applications in near-infrared detectors, as well as in telecommunications, thermoelectric and solar photovoltaic devices (15).

A new synthesis of tetrahedrite-copper antimony sulfide (CAS) nanocrystals ($Cu_{12}Sb_4S_{13}$) that exhibits strong absorption in the visible and NIR is presented here. Through ligand tuning, the size of $Cu_{12}Sb_4S_{13}$ NCs can be increased from 6 to 18 nm. The study also provides information on the detailed study of the optical and photoelectric properties of tetrahedrite ($Cu_{12}Sb_4S_{13}$) and famatinite (Cu_3SbS_4) NCs. (16). Ternary copper-antimony sulfide nanocrystals (CAS NCs) are of increasing interest for use in photovoltaics and photovoltaic nanodevices due to their tunable band gap in the near-IR regime. Considerable progress has been made in the synthesis of CAS NCs. The selective synthesis of CAS NCs with controlled morphologies and compositions is the first (20). In order to study the size-dependent properties of layered materials and to use these materials, intensive research is being done. Copper antimony sulfide ($CuSbS_2$) is a three-layer semiconductor material. This compound has been considered as an absorber material in thin film solar cells due to its high absorption coefficient (>104 cm^{-1}) and band gap (~1.5 eV). For the first time, methods for the synthesis of mono, few and many layers of $CuSbS_2$ were defined (13).

High-quality semiconducting famatinite - Cu_3SbS_4 nanofibers and tetradrite - $Cu_{12}Sb_4S_{13}$ nanoflakes were selectively synthesized by mild hydrothermal and solvothermal synthesis routes, respectively. The morphology and phase of the products can be successfully controlled by choosing the appropriate reaction medium to tune the dynamics of the reaction process. It was determined that the reaction temperature is an important factor affecting the phase purity of the products. This method may provide a general route for the selective preparation of other semiconductor polysulfide nanocrystallites (1). Another work reports extensively on the synthesis of copper-antimony-sulfide (CAS) NCs with different crystal phases, including Cu_3SbS_4, $CuSbS_2$, and $Cu_{12}Sb_4S_{13}$. The properties of compounds in the copper-antimony-sulfide (CAS) system depend on their chemical composition. CAS NC-based devices exhibited diode-like current-voltage characteristics when combined with an n-type CdS layer. In particular, $CuSbS_2$ NC

devices show photovoltaic responses under sunlight (14).

Cu_3SbS_4 nanoparticles are prepared by milling in a laboratory or industrial mill for 120-180 minutes using a protective atmosphere. The composition of the obtained Cu_3SbS_4 samples was confirmed by X-ray phase analysis, and the morphology was confirmed by transmission electron microscopy. Synthesis of Cu_3SbS_4 by mass milling process may be promising for mass production of material with potential photovoltaic properties (4). Cu_3SbS_3 nanowires were obtained by solvothermal method. The phase, morphology, and purity of the products were investigated using X-ray diffraction, transmission electron microscopy, and X-ray photoelectron spectroscopy, respectively. Ethylenediamine is important in the formation of triple sulfides (17). Cu_3SbS_3 nanorods were synthesized under solvothermal conditions with L-cystine. In the experiments, $CuCl_2$ and $SbCl_3$ were used as copper sources. The results showed that Cu_3SbS_3 nanorods are 100-150 nm wide and several micrometers long (8). The authors synthesized tetrahedrite $Cu_{12}Sb_4S_{13}$ using a vibration mill. The processed products are composed of polydisperse nano-sized particles up to 250 nm in size (2). $CuSbS_2$ has been proposed as an absorber material for thin-film solar cells. However, no systematic investigation of the chemical, optical, and electrical properties of $CuSbS_2$ has been conducted. Theoretical and experimental studies have confirmed that $CuSbS_2$ is indeed a very promising absorber material for solar cell applications (21). Tetrahedrite $Cu_{12}Sb_4S_{13}$ has an interesting superstructure based on sphalerite structure. Studies have shown that this tetrahedrite contains two types of copper atoms. The first type is defined by four sulfur atoms at 2.342 A and forms an approximate regular tetrahedron (19). Mechanical alloys of tetrahedrite ($Cu_{12}Sb_4S_{13}$) were synthesized by hot pressing at 723 K for 2 hours under a pressure of 70 MPa. Synthesized tetrahedrite is a non-degenerate semiconductor whose electrical conductivity increased with increasing temperature (10).

In this work, a new solution-based method is proposed for synthesizing copper antimony sulfide nanoparticles by selecting potassium antimony tartrate as an antimony precursor and solution of sulfur in ethylenediamine as a sulfide precursor, which is convenient to use to balance the relative activity of Cu and Sb ions ($SbCl_3$ easily hydrolyzes).

Experimental

Chemical materials. Ethanol, distilled water, ultrapure water, copper (II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$ > 99.99 %), elemental sulfur (99.998 %), ethylene diamine($H_2NCH_2CH_2NH_2$), potassium antimonyl tartrate ($SbOKC_4H_4O_6{\cdot}0.5H_2O$ > 99.99 %), ethylene glycol, and polyethylene glycol ($C_{2n}H_{4n+2}O_{n+1}$ PEG 3000) were used as chemical reagents for the synthesis of copper-antimony-sulfide nanoparticles. In addition, N-heptane (99 %) was used for the preparation of the dispersed solution of nanoparticles.

Instrumental techniques. Thermogravimetric analyzes of the compound obtained under the specified optimal conditions were carried out on a NETZSCH STA 449F349F3 device manufactured in Germany. X-ray phase analysis of the sample was performed on a 2D PHASER Bruker device (CuKα at 0.15418 nm), and its morphology was studied with a scanning electron microscope (HITACHI TM3000). Mass ratios of elements in the compound were determined by chemical analysis (volumetric and gravimetric methods). The study of the optical properties was carried out in the SHIMADZU - UV-5100 (Japan) spectrophotometer.

Synthesis of Cu_3SbS_4 compound. For the synthesis of the compound Cu_3SbS_4, the amounts of copper (II) chloride and potassium antimonyl tartrate were taken in stoichiometric proportions (Cu:Sb = 1 : 1) and dissolved in ethylene glycol. In another test vessel, a transparent solution was prepared by dissolving elemental sulfur in ethylenediamine (elemental sulfur dissolves very easily in ethylenediamine). After both solutions are mixed, they are collected in a 50 ml Teflon cuvette, and after adding a solution of polyethylene glycol in ethanol equal to the volume of ethylene glycol, the cuvette mouth is closed. The volume of the final solution should be 75–80 % of the volume of the cuvette. The Teflon cuvette is kept in a heater at a temperature of 393 K for 15 hours. Then the heater is allowed to cool down to room temperature. The obtained nanoparticles were washed with ethanol and centrifuged (Heraeus Thermo Scientific). The centrifugation products were collected together, washed with ethyl alcohol, and then dried in a vacuum at a temperature of 333K for one hour.

Results and discussion

Thermogravimetric analysis. The thermogravimetric analysis (TG) of the (Cu_3SbS_4) compound obtained under the specified optimal

conditions was performed on a NETZSCH STA 449F349F3 device manufactured in Germany. 15.6 g of the sample was heated to a temperature of 1100 K in the air (O_2, N_2) (air supply rate 30 ml/min). Derivatogram of the analysis is presented in Figure 1.

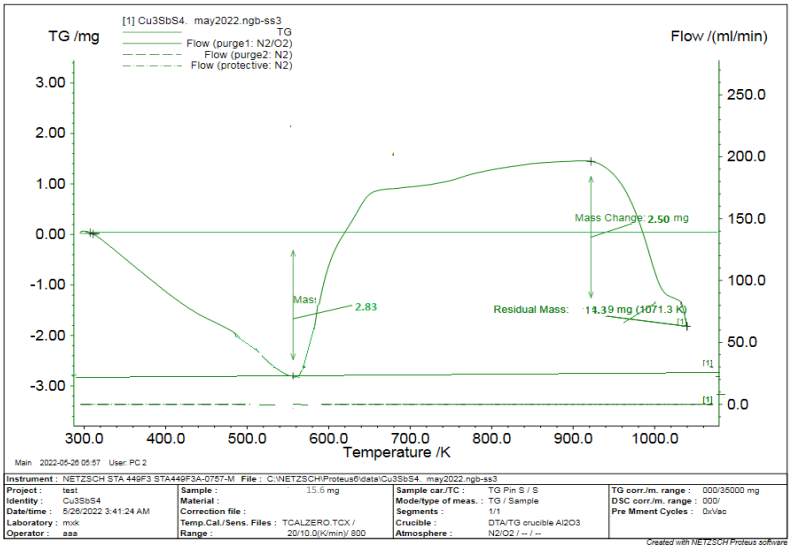

Fig. 1. Dervatogram of nanoparticles of Cu_3SbS_4

According to theoretical calculations, sulfur is 4.51 mg in a 15.6 mg sample (Cu_3SbS_4). Oxidation of antimony-bound sulfur occurs in an oxygen environment. This process ends at 573 K. From the X-ray phase analysis, we determined the residue remaining at 573 K. According to the results of XRD analysis, it was found that oxidation of CuS to $CuSO_4$ occurs at T > 573 K.

Experimentally, since the mass of the sample decreased by 2.83 mg at a temperature of 573 K, it can be said that this loss is sulfur. In the results of some works up to now, it is noted that similar results were obtained in the thermogravimetric analysis of the Cu_3SbS_4 compound. A combination of Sb_2O_3 and $CuSO_4$ was found in the main composition of the residue at 1100 K. At subsequent temperatures, the mass of the sample increased. The composition of decomposition products obtained in the temperature range of 300–1100 K was confirmed by X-ray phase analysis. The mass of the sample increased in the temperature range of 573–940 K. This mass increase occurred due to oxidation of antimony and copper. It was determined that the mass loss of 2.83 mg (the theoretical mass of sulfur is 4.51 mg) was due to sulfur in the share of antimony. The sulfur corresponding to copper was converted into copper(II) sulfate during oxidation.

$$CuS + 2O_2 = CuSO_4 \quad (1)$$

The mass loss that reappeared in the temperature interval of 940-1100 K was due to the decomposition of copper(II) sulfate.

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

Theoretically, the total oxides formed by antimony and copper in the sample is 14.41 mg. The mass of the experimentally formed residue was 14.39 mg, which are approximately equal to each other. At the same time, the residue was also chemically analyzed and the obtained results show that the formula of the sample corresponds to copper antimony sulfide (Cu_3SbS_4).

Chemical analysis. Copper thiostibiate samples were chemically analyzed according to the methodology given below: a known amount of Cu_3SbS_4 sample is dissolved in nitric acid by heating. The solution is diluted and made up to a known volume. In separate samples, antimony is determined gravimetrically, copper is determined by the iodometric (volumetric) method, and sulfur is determined in the form of sulfate ion (11). The results are given in Table 1.

Table 1

Chemical analysis of copper (I) thiostibiate

Sample, g	Amount of elements, g					
	Cu		Sb		S	
0.4417	Theor.	Exper.	Theor.	Exper.	Theor.	Exper.
	0.1920	0.1907	0.1217	0.1183	0.1280	0.1244

The results of the analysis showed that the experimental values of Cu, Sb and S elements in the sample correspond approximately to their theoretical values. This indicates that the

Journal of Chemistry and Technologies, 2024, *32*(2), 304-311

composition of the compound corresponds to the formula Cu_3SbS_4.

XRD Analysis. The X-ray phase analysis of copper thiostibiate obtained in organic medium was carried out on a 2D PHASER Bruker powder diffractometer (CuKα, λ = 1.5406 Å, 0 < 2θ < 700) and its diffractogram was drawn (Fig. 2).

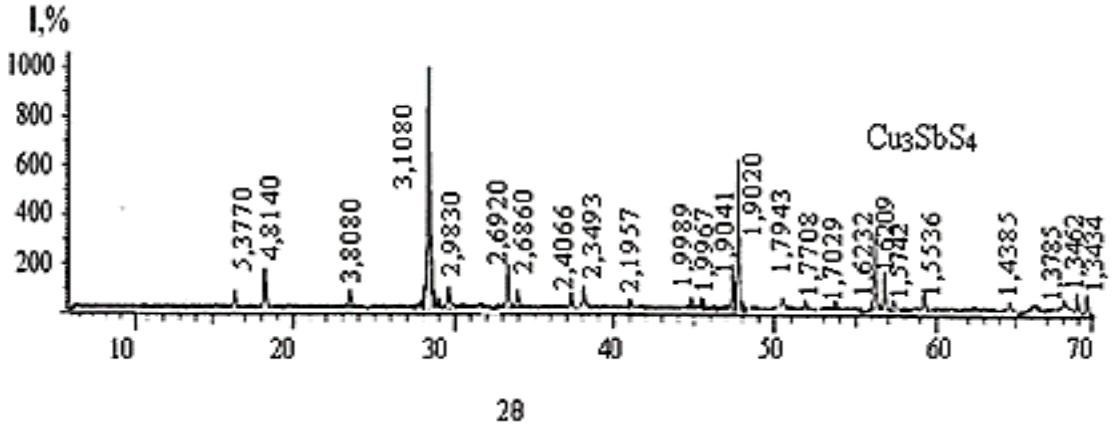

Fig. 2. Diffractogram of copper thiostibiate nanocomposite

The structural arrangement obtained based on the diffractogram of the Cu_3SbS_4 sample is well consistent with its (JCPDS # 01-071-0555) reference value. Crystallographic data of Cu_3SbS_4 showed that it has a tetragonal structure (cryst. group, a = 5.38500 Å and c = 10.75400 Å). These results confirm that famatinite (Cu_3SbS_4) does not have another crystalline phase.

EDS analysis. In order to determine the stoichiometric composition of the copper thiostibiate nanocompound, the elemental analysis of the composition of the obtained compound was carried out on a Oxford Instrument - JSM-6610LV SEM device. The results of the analysis are given in figure 3.

Element	Çəki %	Atom %
S	17.25	30.18
Cu	75.07	66.28
Sb	7.68	3.54
Cəm	100.00	

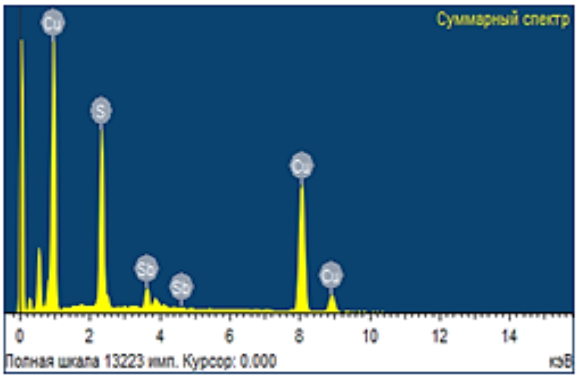

Fig. 3. Elemental analysis of the composition of the compound

It is known that the EDS system is a source of high-energy radiation. The impact of high-energy electrons on the surface of the sample causes the separation of radiation rays in the form of energy when electrons are detached

from the surface and their place is filled with other electrons. This energy release allows the compositional analysis (identification) of the sample. Thus, the position of the peaks in the spectrum determines the element, and the intensity of the signal corresponds to the concentration of the element. From the results of the analysis, it is known that the sample consisted of a combination of Cu, Sb, and S atoms, which confirms its individuality.

SEM analysis. Morphology of Cu_3SbS_4 nanoparticles. Microstructural analysis of Cu_3SbS_4 samples synthesized in organic medium (EG +PEG) at temperatures of 383-393K for 12 hours was performed on a Hitachi TM3000 electron microscope. Copper (II) chloride was used in experiments to obtain copper thiostibiate. This is due to its easy availability, cheapness and solubility in ethyl alcohol. As a sulphiding reagent, a solution of sulfur in ethylenediamine acts both as a surfactant and as a reducing agent. At the same time, it is less harmful than other sulfidizing reagents, and it is possible to prepare a solution of sulfur at any concentration. Microphotos of the sample are given in figure 4.

Journal of Chemistry and Technologies, 2024, *32*(2), 304-311

Increasing the proportion of ethylenediamine has a positive effect on the formation of nanoparticles. The -NH_2 group in ethylenediamine interacts with metal ions and participates in the formation of nanoparticles. Ligand molecules attached to the surface of nanoparticles not only control the growth and synthesis of particles, but also prevent nanoparticle aggregation. Copper ions create Cu-N coordination and allow controlling the growth rate of the ligand molecule. In addition, during the nanoparticle growth phase, the surfactant reduces the surface tension and prevents aggregation through the repulsive force between the particles.

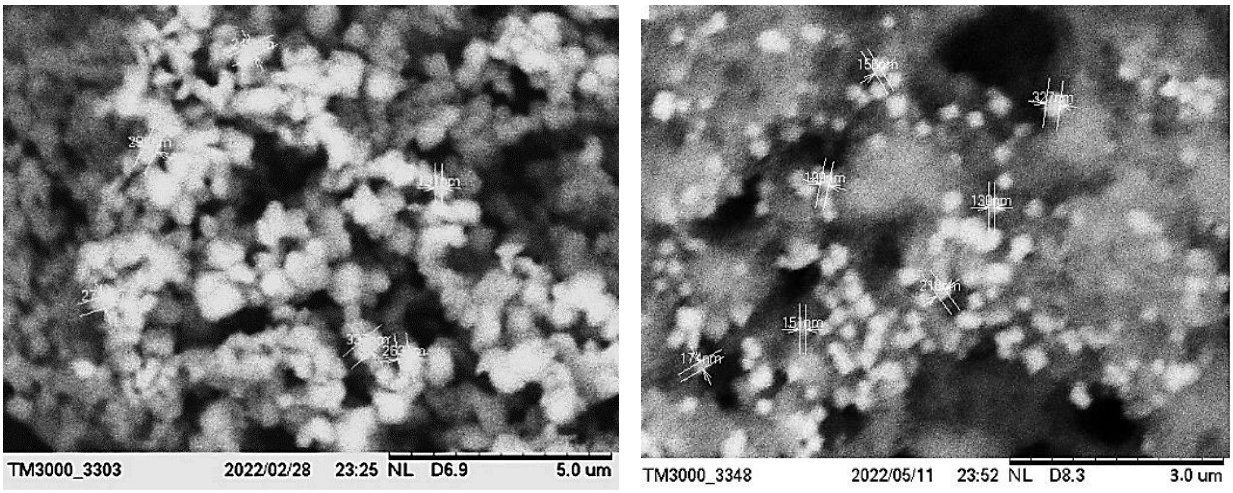

Fig. 4. Micromorphology of Cu_3SbS_4 nanoparticles, magnification limit, a) 5 µm, b) 3 µm

These compounds are mostly in amorphous state. SEM analysis revealed that the particles in the copper thiostibiate compound obtained in ethylene glycol medium had spherical and cubic structures connected to each other, and no other phase particles were observed between the particles in the area of 5 and 3 µm. The size of the particles varies between 130–310 nm.

Optical properties of copper antimony sulfide. A certain amount of copper thiostibiat dispersed solution 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 on a U-5100 Hitachi ultraviolet spectrophotometer, the optical absorption curve was shown at figure 5, and dependencies were established.

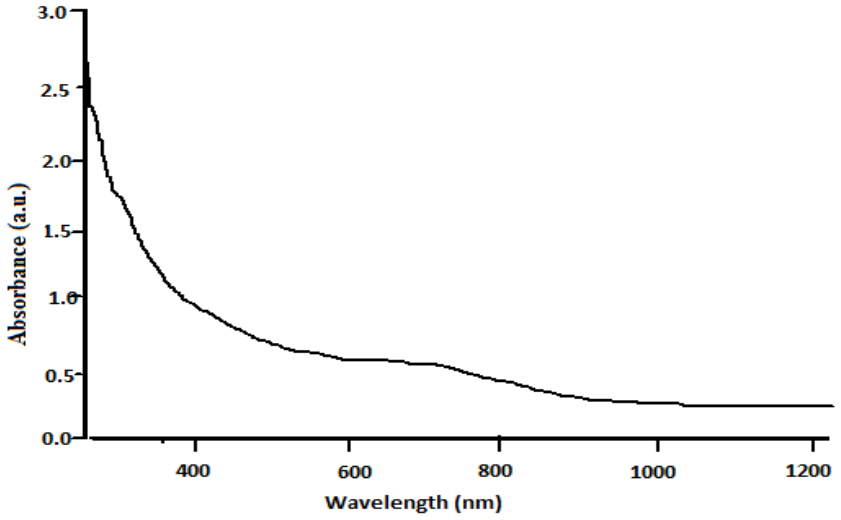

Fig. 5. Absorption spectrum of a dispersed solution of copper thiostibiate

It is known that the width of the forbidden energy gap of solutions and thin films of semiconductor compounds can be calculated by the Tauch formula:

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

where A – is a constant number, E_g – is the forbidden energy gap width of the semiconductor, $\hbar\nu$ – is the energy of the photon. n can take four different values

Journal of Chemistry and Technologies, 2024, *32*(2), 304-311

depending on the type of transition. Thus, n=1/2 for a permitted straight transition, n=2 for a permitted left transition, n=3/2 for a forbidden straight transition, and n=3 for a forbidden left transition take values. Based on the obtained values, the dependence curve of $(\alpha h\nu)^2$ on hν was established and the value of the width of the forbidden energy gap of the combination was determined.

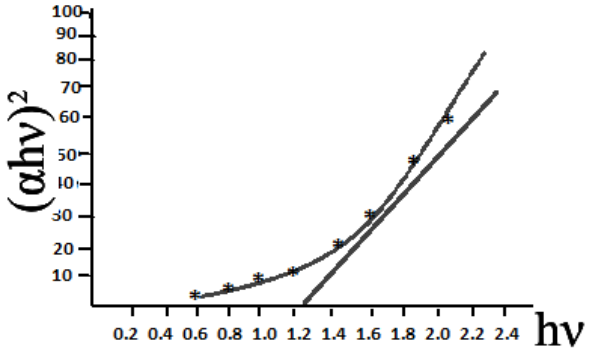

Fig. 6. Graph of dependence of $(\alpha h\nu)^2$ - hν nanoparticles of Cu_3SbS_4

As can be seen from the graph, the forbidden energy gap width of Cu_3SbS_4 nano compound synthesized by solvothermal method was equal to Eg = 1.25 eV. In the literature, the width of the forbidden energy gap of the thin layer of fematinite takes different values (0.85–1.2 eV) depending on the conditions of acquisition.

Conclusion

Cu_3SbS_4 nanocrystals were synthesized under easy conditions by solvothermal method in organic medium (EG+PEG) and with the help of ethylenediamine. The optimal conditions for obtaining nanoparticles have been determined (molar ratios of the amount of components, volume ratio of the solvent, temperature, etc.). By thermogravimetric, EDS and chemical analysis, it was determined that the composition of copper thiostibiate nanocomposite corresponds to the Cu_3SbS_4 formula. The structure (individuality) of the sample was confirmed by RFA, the morphology was studied by an electron microscope and pictures of the nanoparticles were taken. A dispersed solution of Cu_3SbS_4 nanoparticles in n-heptane was prepared, and the width of the forbidden energy gap was found based on the absorption spectrum of the solution. With the proposed method, Cu_3SbS_4 nanoparticles are easily synthesized at low temperature (120 ℃) and with high yield (85 %). We believe that thin layers of Cu_3SbS_4 nanoparticles can be prepared by using an ultrasonic homogenizer to obtain a homogeneous solution of smaller particles.

Acknowledgment

The author wants to thank the Institute of Natural Resources of the Ministry of Science and Education of the Republic where the whole physicochemical analyses were performed.

Conflict of interest

The author declares no conflict of interest.

References

[1] An, C., Jin, Y.,Tang, K., Qian, Y. (2003). Selective synthesis and characterization of famatinite nanofibers and tetrahedrite nanoflakes. *Journal of Materials Chemistry, 13*(2), 301–3.

[2] Baláž, P., Guilmeau, E., Daneu, N., Dobrozhan, O., Baláž, M., Hegedus, M., Barbier, T., Achimovičová, M., Kaňuchová M., Briančin, J. (2020). Tetrahedrites synthesized via a scalable mechanochemical process and spark plasma sintering. *Journal of the European Ceramic Society, 1, 40*(5), 1922–30.

[3] Bella, M., Rivero, C., Blayac, S., Basti, H., Record, M.C., Boulet,P. (2017). Oleylamine-assisted solvothermal synthesis of copper antimony sulfide nanocrystals: Morphology and phase control. *Materials Research Bulletin, 90*, 188–94.

[4] Dutková, E., Sayagués, M.J., Fabián, M., Baláž, M., Achimovičová, M. (2021). Mechanochemically synthesized ternary chalcogenide Cu_3SbS_4 powders in a laboratory and an industrial mill. *Materials Letters. 291*, 129566.

[5] Fernandes, P.A., Shongalova, A., da Cunha, A.F., Teixeira, J.P., Leitão, J.P., Cunha, J.M., Bose, S., Salome, P.M., Correia, M.R. (2019). Phase selective growth of $Cu_{12}Sb_4S_{13}$ and Cu_3SbS_4 thin films by chalcogenization of simultaneous sputtered metal precursors. *Journal of Alloys and Compounds, 797*, 1359–66.

[6] Gur, I., Fromer, N.A., Geier, M.L., Alivisatos, A.P. (2005). Air-stable all-inorganic nanocrystal solar cells processed from solution. *Science, 310*(5747), 462–5.

[7] Jasieniak, J., MacDonald, B.I., Watkins, S.E., Mulvaney, P. (2011). Solution-processed sintered nanocrystal solar cells via layer-by-layer assembly. *Nano letters, 11*(7), 2856–64.

[8] Jiasong, Z., Weidong, X., Huaidong, J., Wen, C., Lijun, L., Xinyu, Y., Xiaojuan, L., Haitao, L. (2010). A simple L-cystine-assisted solvothermal approach to Cu_3SbS_3 nanorods. *Materials Letters, 64*(13), 1499–502.

[9] Kamat, P.V. (2008). Quantum dot solar cells. Semiconductor nanocrystals as light harvesters. *The Journal of Physical Chemistry C, 112*(48), 18737–53.

[10] Kim, S.Y., Kwak, S.G., Pi, J.H., Lee, G.E., Kim, I.H. (2019). Preparation of tetrahedrite $Cu_{12}Sb_4S_{13}$ by mechanical alloying and hot pressing. *Journal of Electronic Materials, 48*(4), 1857–63.

[11] Korostelev, P.P. (1985). *Gravimetric and titrimetric analysis in metallurgy*. Handbook. Moscow, Metallurgy.

[12] Poudel, B., Hao, Q., Ma, Y., Lan, Y., Minnich, A., Yu, B., Yan, X., Wang, D., Muto, A., Vashaee, D., Chen, X. (2008). High-thermoelectric performance of nanostructured bismuth antimony telluride bulk alloys. *Science, 320*(5876), 634–8.

[13] Ramasamy, K., Sims, H., Butler, W.H., Gupta, A. (2014). Mono-, few-, and multiple layers of copper antimony sulfide ($CuSbS_2$): a ternary layered sulfide. *Journal of the American Chemical Society, 136*(4), 1587–98.

[14] Suehiro, S., Horita, K., Yuasa, M., Tanaka, T., Fujita, K., Ishiwata, Y., Shimanoe, K., Kida, T. (2015). Synthesis of copper–antimony-sulfide nanocrystals for solution-processed solar cells. *Inorganic chemistry, 54*(16), 7840–5.

[15] Van Embden, J., Tachibana, Y. (2012). Synthesis and characterisation of famatinite copper antimony sulfide nanocrystals. *Journal of Materials Chemistry, 22*(23), 11466–9.

[16] Van Embden, J., Latham, K., Duffy, N.W., Tachibana, Y. (2013). Near-infrared absorbing $Cu_{12}Sb_4S_{13}$ and Cu_3SbS_4 nanocrystals: synthesis, characterization, and photoelectrochemistry. *Journal of the American Chemical Society, 135*(31), 11562–71.

[17] Wang, M.X., Yue, G.H., Fan, X.Y., Yan, P.X. (2008). Properties and characterization of Cu_3SbS_3 nanowires synthesized by solvothermal route. *Journal of crystal growth, 310*(12), 3062–6.

[18] Wang, R.Y., Feser, J.P., Lee, J.S., Talapin, D.V., Segalman, R., Majumdar, A. (2008). Enhanced thermopower in PbSe nanocrystal quantum dot superlattices. *Nano letters, 8*(8), 2283–8.

[19] Wuensch, B.J. (1964). The crystal structure of tetrahedrite, $Cu_{12}Sb_4S_{18}$. *Zeitschrift für Kristallographie-Crystalline Materials, 119*(1-6), 437–53.

[20] Xu, D., Shen, S., Zhang, Y., Gu, H., Wang, Q. (2013). Selective synthesis of ternary copper–antimony sulfide nanocrystals. *Inorganic chemistry, 52*(22), 12958–62.

[21] Yang, B, Wang, L., Han, J., Zhou, Y., Song, H., Chen, S., Zhong, J., Lv, L., Niu, D., Tang, J. (2014). $CuSbS_2$ as a promising earth-abundant photovoltaic absorber material: a combined theoretical and experimental study. *Chemistry of Materials, 26*(10), 3135–43.