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# PRODUCTION OF NANOPARTICLES OF $AgAsS_2$ AND $Ag_3AsS_3$ COMPOUNDS

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*Synthesis of ternary sulfides $AgAsS_2$ and $Ag_3AsS_3$ from systems $AgNO_3 - As_2S_3$, $AgNO_3 - NaAsO_2 - Na_2S$ and $AgNO_3 - As_2S_3 - HNO_3$ in ethylene glycol medium, obtained nano- and microparticles of compounds, their physicochemical properties studied. The solution stirred for 30 minutes, poured into an experimental bowl, placed in a Teflon cuvette, sealed and placed in a microwave electric heater and heated for a day at a temperature of 373-453 K. After synthesis, the precipitate filtered. For extraction, excess of arsenic washed with 0.1 M nitric acid solution, distilled water and ethanol. The purified precipitate dried at 353 K for 1 hour. It has been established that at pH = 4-6 and molar ratios of the initial components $AgNO_3 : As_2S_3 = 3:2$ and $AgNO_3 : As_2S_3 = 3:1$, $AgAsS_2$ and $Ag_3AsS_3$ compounds, respectively, are obtained. At 373-453 K, nanoparticles formed, the size of which varies depending on the temperature and duration of heat treatment. The individuality of the synthesized compounds controlled by differential thermal and X-ray diffraction methods of analysis. According to the DTA results, the $AgAsS_2$ and $Ag_3AsS_3$ compounds revealed two endothermic effects. The endothermic effect observed at 695 ± 2 K and 763 ± 2 K corresponds to the melting temperature of the $AgAsS_2$ and $Ag_3AsS_3$ compounds, respectively. The endothermic effect observed at 594 K and 465 K corresponds to a polymorphic transition. According to SEM data, it found that the synthesized compound has nano- and microsizes at 413-433 K. The sizes and shapes of nanoparticles and microparticles vary depending on conditions, temperature and pH.*

***Keywords:*** *organic solvent, silver (I) nitrate, nanoparticles, thioarsenites, sediment.*
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## INTRODUCTION

The continuous search and study of new nanoscale materials is an important factor in the development of modern science and technology. Silver (I) thioarsenites ($AgAsS_2$ and $Ag_3AsS_3$) are among the important functional materials of modern technology. Most compounds of this class widely used and considered promising materials with valuable semiconductor, photo-, ferroelectric-, and thermoelectric properties [1, 2].

Synthesis of silver nanoparticles briefly, 5 mL of sodium citrate 0.05 M (TSC, Sigma-Aldrich CAS 6132-04-3) and 5 mL of silver nitrate 0.05 M ($AgNO_3$, PANREAC CAS 7761-88-8) added to 185 mL of water type 1 in a cold bath between 6°C to 10°C. The solution stirred for 3 min at 3000 RPM. Subsequently, 5 mL of sodium borohydride 0.05 M ($NaBH_4$, Sigma-Aldrich CAS 16940-66-2) dripped slowly. The pH adjusted to 10 with sodium hydroxide 1.25 M (NaOH, PANREAC CAS 1310-73-2). The nanoparticles obtained were stored in amber bottles at 4°C. These nanoparticles were the reference AgNPs (Ref-AgNPs) for the study [3-9].

In the $Ag_2S - As_2S_3$ system known compounds with compositions of $AgAsS_2$ and $Ag_3AsS_3$. These compounds possess unique semiconductor properties [10, 11]. $AgAsS_2$ compound melts at 696 K, polymorphic transformation occurs at 594 K, and according to [10], at the low-temperature modifi-

cation (trechmannite) (T < 594 K) crystallizes in the orthorhombic (sp. gr. $R\bar{3}$ : $a$ = 1.398, $c$ = 0.912 nm ), and at the high-temperature modification (smithite) – in the hexagonal (sp. gr. $A2/a$ : $a$ = 1.723, $b$ = 0.778, $c$ = 1.519 nm; β = 101,2°) structures [12, 13, 14]. This compound decomposes at a temperature above 773 K.

The compound of $Ag_3AsS_3$ melts at 764 K, its polymorphic transformation occurs at 468 K. The low-temperature modification (xanthoconite) (T < 468 K) crystallizes in the orthorhombic (sp. gr. $C2/c$ : $a$ = 1.200, $b$ = 0.626, $c$ = 1.708 nm; β = 110°), and the high temperature modification (proustite) – in the hexagonal (sp. gr. $R3c$ : $a$ = 1.083, $c$ = 0.865 nm; β = 103.52°) structures [12, 13].

From the literature [10, 11] it is known that silver thioarsenites are synthesized at high temperatures (700-800 K) in deaerated (~$10^{-2}$ Pa) quartz ampoules by melting the elemental components or silver (I) sulfide with arsenic (III) sulfide. To homogenize these compounds is required high temperature and too much time. In this regard, the production of silver (I) thioarsenites in solution at low temperatures is one of the most urgent matters. It known that the production of d-metal chalcogenides in polar and low-polarity organic solvents is of great practical importance recently, since impurities are less in composition of the compounds obtained in an organic solvent medium. Furthermore, the formation of nanoparticles and microparticles is very easy. Information on the production of silver (I) thioarsenites in ethylene glycol medium is almost absent in the literature. Ethylene glycol is a colorless, viscous, hygroscopic, odorless liquid with sweetish taste. Its boiling point is 470.6 K, melting temperature 287.5 K, density 1.1132 g/cm$^3$. It is soluble in water, alcohols, and ketones, et al., mildly soluble in benzene, toluene, and diethyl ether. Aqueous solutions of ethylene glycol freeze at low temperatures (down to -343 K). It forms partial and full ethers with monobasic acids. Ethylene glycol used in many industries: chemical, motorcar, aerospace, electrical, textile, oil and gas and others. One of ethylene glycol main applications is the production of nonfreezable fluids, cooling, and heat-transfer agents. Ethylene glycol is use as solvent, as starting reagent in the chemical industry for the production of many inorganic compounds, synthetic resins, and polymers, in the manufacturing of polyurethanes, explosive, and odoriferous substances. The dielectric constant at 293 K is equal to 37.0 [3, 6, 15, 16]. Consider this, in the synthesis of $Ag_3AsS_3$ and $AgAsS_2$ compounds we used ethylene glycol as the solvent.

The study results of $AgAsS_2$ and $Ag_3AsS_3$ compounds nanoparticles obtaining conditions in ethylene glycol medium are cite in this paper.

**MATERIAL AND METHODS**

To obtain $AgAsS_2$ and $Ag_3AsS_3$ compounds nanoparticles in ethylene glycol medium are investigated physical and chemical interactions within the system of the $AgNO_3 - As_2S_3$, $AgNO_3 - NaAsO_2 - Na_2S$ and $AgNO_3 - As_2S_3 - HNO_3$.

As starting components in the $AgNO_3 - As_2S_3$ system were used $AgNO_3$ and $As_2S_3$. $As_2S_3$ and $AgNO_3$ were taken in a molar ratio, according to the reaction equation, mixed, and 20 ml of ethylene glycol were added to this mixture. The solution was stirred for 30 minutes, and then each sample was transferred to 2 autoclaves and heated for 24 hours at temperatures of 373-453 K. After synthesis, the precipitate filtered. For extraction, the excess of arsenic washed with 0.1 M of nitric acid solution, distilled water and ethanol. The purified precipitate dried at 353 K for 1 hour. The composition of the obtained compounds determined by NETZSCH STA 449F349F3 derivatograph (Germany) and chemical analysis. Differential thermal analysis (DTA) carried out in an HTP-70 pyrometer, Thermoscan-2 device, in an inert atmosphere. The phase analysis of $AgAsS_2$ and $Ag_3AsS_3$ nano- and microparticles was studied using a Bruker D8 ADVANCE X-ray diffractometer (CuKα, λ = 1.5406 Å, 0 < 2θ < 80º). Morphological studies performed using scanning electron microscopy

TM3000 (Hitachi, Japan), also studied the influence of pH medium (pH METER-pH410 "AKVILON").

**RESULTS AND DISCUSSION**

The resulting precipitate investigated by microstructure analysis. It ascertained that the nanoparticles (Figure 1) formed at 373-453 K. In practice, it ascertained that sizes of nanoparticles vary depending on the temperature and heat treatment time.

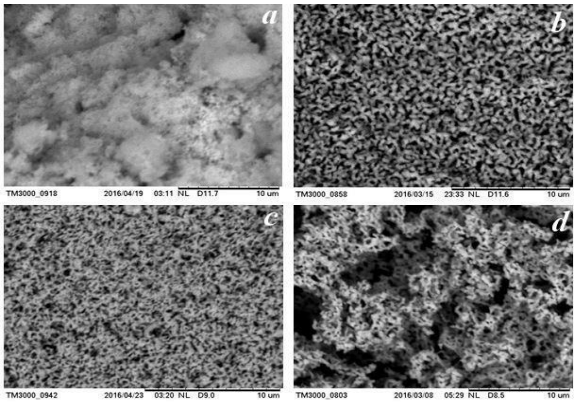



**Fig. 1.** The photomicrograph of nanoparticles of $AgAsS_2$ (*a* – at 373 K; *b* – at 453 K) and $Ag_3AsS_3$ (*c* – at 373 K; *d* – at 453 K) compounds.

The individuality of the synthesized compounds monitored by methods of differential thermal analysis (Figure 2).

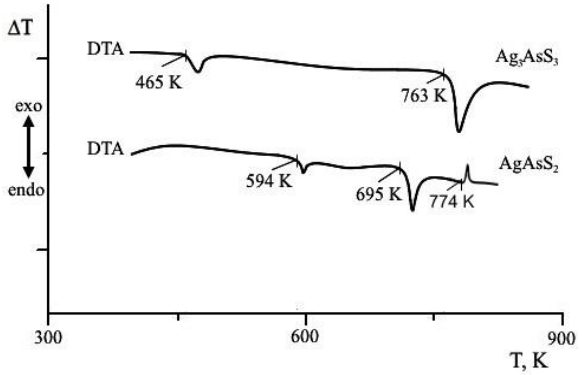



**Fig. 2.** The DTA curve of $Ag_3AsS_3$ and $AgAsS_2$ compounds.

In the DTA curve (Figure 2) of $AgAsS_2$ and $Ag_3AsS_3$ compounds found two endothermic effects. The endothermic effect observed at 695 ± 2 K and 763±2 K corresponds to the melting point of $AgAsS_2$ and $Ag_3AsS_3$ compounds, respectively. The endothermic effect observed at 594 K and 465 K corresponds to the polymorphic transition of $AgAsS_2$ and $Ag_3AsS_3$ compounds that agrees well with the published data, presented above. In this paper has been studied also the influence of pH medium and temperature on total precipitation of $AgAsS_2$ and $Ag_3AsS_3$ compounds. For production in an acid medium solution, we used hydrochloric acid and monitored product yield at different pH values of medium in the temperature range of 353-453 K. It has been ascertained that the maximum yield of $AgAsS_2$ and $Ag_3AsS_3$ compounds is observed at pH = 4 and at the temperature of 393 K. According to XRD data it has been found that at pH >7 a mixture of products: $Ag_3AsO_3$, $H_3AsO_3$, $Ag_2S$

и $AgAsS_2$ ($Ag_3AsS_3$) is formed in the system. $AgAsS_2$ and $Ag_3AsS_3$ compounds decompose at pH < 2. Effect of medium pH and temperature on complete precipitation of $AgAsS_2$ and $Ag_3AsS_3$ compounds represented in the following table 1.

**Table 1.**

The study results of medium pH and temperature effect on the yield of $AgAsS_2$ and $Ag_3AsS_3$ compounds.

| The temperature, K | pH | Compound yield, % | |
|---|---|---|---|
| | | $AgAsS_2$ | $Ag_3AsS_3$ |
| 343 | 3.5 | 93.31 | 92.59 |
| 373 | 3.8 | 94.67 | 95.52 |
| 393 | 4 | 96.94 | 97.68 |
| 435 | 5 | 96.64 | 95.49 |
| 453 | 6 | 95.32 | 95.13 |

In the $AgNO_3 - NaAsO_2 - Na_2S$ system at the synthesis of $AgAsS_2$ and $Ag_3AsS_3$ compounds in ethylene glycol medium we used $AgNO_3$, $NaAsO_2$ and $Na_2S$ as starting components. According to the reaction equation:

$$AgNO_3 + NaAsO_2 + 2Na_2S + 4HNO_3 \rightarrow AgAsS_2 + 5NaNO_3 + 2H_2O;$$
$$3AgNO_3 + NaAsO_2 + 3Na_2S + 4HNO_3 \rightarrow Ag_3AsS_3 + 7NaNO_3 + 2H_2O$$

We mixed $NaAsO_2$ and $AgNO_3$ with $Na_2S$ in ethylene glycol medium in molar ratios of $AgNO_3 : NaAsO_2 : Na_2S = 1:1:2$ and $AgNO_3 : NaAsO_2 : Na_2S = 3:1:3$, respectively. Synthesis carried out in the temperature range of 413-433 K for 24 hours. According to SEM HITACHI TM3000 data it is ascertained that the synthesized compound is nano- and micro-sized at 413-433 K. Sizes and shapes of nano- and microparticles vary depending on the conditions, temperature and pH = 4-5 (Figure 4.).

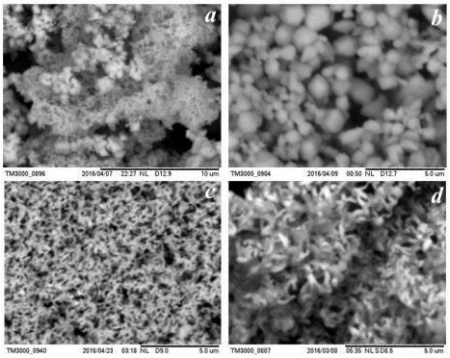
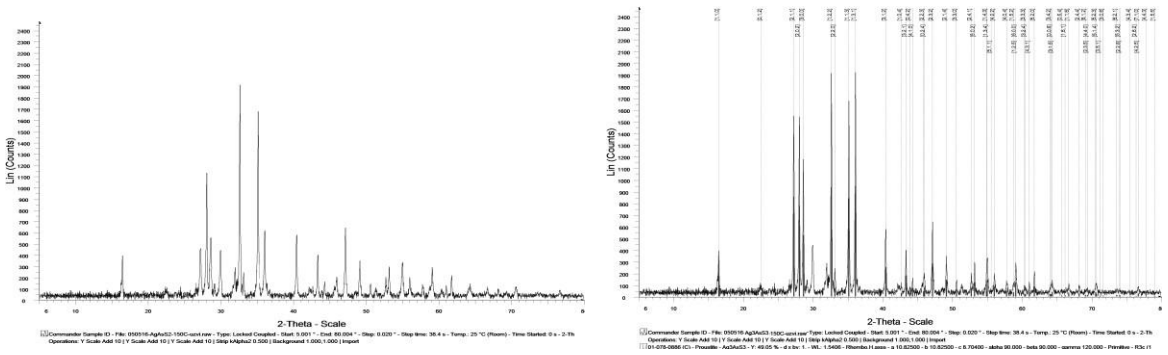



**Fig. 4.** The photomicrograph of nanoparticles of $AgAsS_2$ (*a* – at 413 K; *b* – at 433 K) and $Ag_3AsS_3$ (*c* – at 413 K; *d* – at 433 K) compounds

Based on the XRD data, it determined that at 453 K $AgAsS_2$ (a) and $Ag_3AsS_3$ (b) compounds obtained in the system (Figure 5 a, b).




a) b)

**Fig. 5.** The diffraction pattern of $AgAsS_2$ (a) and $Ag_3AsS_3$ (b) compounds obtained at 453 K (a).

In the $AgNO_3 - As_2S_3 - HNO_3$ system depending on molar ratios of $AgNO_3$, $As_2S_3$ and $HNO_3$ are obtained $Ag_3AsS_3$ and $AgAsS_2$ compounds in ethylene glycol medium. Practically it found that in ethylene glycol medium, in molar ratios of $AgNO_3 : As_2S_3 : HNO_3 = 1:1:7$ obtained $AgAsS_2$ compound, and in $AgNO_3 : As_2S_3 : HNO_3 = 5:12:18$ – $Ag_3AsS_3$ compound.

$$As_2S_3 + AgNO_3 + 7HNO_3 \rightarrow AgAsS_2 + H_3AsO_4 + 8NO_2 + SO_2 + 2H_2O$$
$$5As_2S_3 + 12AgNO_3 + 18HNO_3 \rightarrow 4Ag_3AsS_3 + 6H_3AsO_4 + 30NO_2 + 3SO_2$$

## CONCLUSION

Very simple synthetic methods developed for the preparation of $AgAsS_2$ and $Ag_3AsS_3$ chalcogenides in ethylene glycol medium without polluting the environment. Nanoparticles of $AgAsS_2$ and $Ag_3AsS_3$ compounds have been obtained in the systems of $AgNO_3 - As_2S_3$, $AgNO_3 - NaAsO_2 - Na_2S$ and $AgNO_3 - As_2S_3 - HNO_3$ The effect of temperature, time and pH on the complete formation of nanoparticles of these compounds studied. During the conducted research, it was determined that nanoparticles are obtained in the system of $AgNO_3 - NaAsO_2 - Na_2S$ at a temperature range of 453 K within 24 hours (pH = 4-5)

## ACKNOWLEDGEMENTS

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## $AgAsS_2$ VƏ $Ag_3AsS_3$ BİRLƏŞMƏLƏRİNİN NANOHİSSƏCİKLƏRİNİN ALINMASI

**T.İ. Süleymanova**

$AgAsS_2$ və $Ag_3AsS_3$ üçlü sulfidlərin $AgNO_3 - As_2S_3$, $AgNO_3 - NaAsO_2 - Na_2S$ və $AgNO_3 - As_2S_3 - HNO_3$ sistemlərindən etilenqlikol mühitində sintezi, alınan birləşmələrin nano- və mikrohissəcikləri, onların fiziki-kimyəvi xassələri tədqiq edilmişdir. Məhlul 30 dəqiqə qarışdırılır, təcrübə qabına tökülür, teflon kyuvetə yerləşdirilir, ağzı kip bağlanır və mikrodalğalı elektrik qızdırıcısına qoyulur. Bir gün ərzində 373-453 K temperaturda qızdırılır. Sintezdən sonra çöküntü süzülür, ekstraksiya üçün artıq arsen 0,1 M azot turşusu məhlulu, distillə edilmiş su və etanol ilə yuyulur. Təmizlənmiş çöküntü 1 saat ərzində 353 K-də qurudulur. Müəyyən edilmişdir ki, , ilkin komponentlərin $AgNO_3 : As_2S_3 = 3:2$ və $AgNO_3 : As_2S_3 = 3:1$ mol nisbətində və pH = 4-6 qiymətlərində müvafiq olaraq birləşmələr əldə edi-

lir. 373–453 K-da nanohissəciklər əmələ gəlir, hissəciklərin ölçüləri temperaturdan asılı olaraq dəyişir. Sintez edilmiş birləşmələrin fərdiliyi diferensial istilik və rentgen şüalanma analiz üsulları ilə müəyyən olunmuşdur. DTA nəticələrinə görə birləşmələrin iki endotermik təsiri aşkar edilmişdir. 695 ± 2 K və 763 ± 2 K-də müşahidə olunan endotermik təsir müvafiq olaraq birləşmələrin ərimə nöqtəsinə uyğundur. 594 K və 465 K-də müşahidə edilən endotermik təsir polimorfik keçidə uyğundur. SEM məlumatlarına əsasən, sintez edilmiş birləşmənin 413–433 K-də nano- və mikroölçülərə malik olduğu aşkar edilmişdir. Nanohissəciklərin və mikrohissəciklərin ölçüləri və formaları şəraitdən, temperaturdan və pH-dan asılı olaraq dəyişir.

**Açar sözlər:** *üzvi həlledici, gümüş (I) nitrat, nanohissəciklər, tioarsenitlər, çöküntü.*

## ПОЛУЧЕНИЕ НАНОЧАСТИЦ СОЕДИНЕНИЙ $AgAsS_2$ И $Ag_3AsS_3$

**Т.И. Сулейманова**

Синтез тройных сульфидов $AgAsS_2$ и $Ag_3AsS_3$ из систем $AgNO_3 - As_2S_3$, $AgNO_3 - NaAsO_2 - Na_2S$ и $AgNO_3 - As_2S_3 - HNO_3$ в среде этиленгликоля, полученные нано- и микрочастицы соединений, изучены их физико-химические свойства. Раствор перемешивали в течение 30 минут и переливали в экспериментальную чашу, помещали на тефлоновую кювету, герметизировали и помещали в микроволновый электронагреватель и нагревали в течение суток при температуре 373-453 К. После синтеза осадок фильтруют. Для экстракции избыток мышьяка промывают 0,1 М раствором азотной кислоты, дистиллированной водой и этанолом. Очищенный осадок сушили при 353 К в течение 1 часа. Установлено, что при pH = 4-6 и мольных соотношениях исходных компонентов $AgNO_3 : As_2S_3 = 3:2$ и $AgNO_3 : As_2S_3 = 3:1$ соответственно получаются соединения $AgAsS_2$ и $Ag_3AsS_3$. При 373-453 К образуются наночастицы, размер которых меняется в зависимости от температуры и продолжительности термообработки. Индивидуальность синтезированных соединений контролируют дифференциально-термическим и рентгеноструктурным методами анализа. По результатам ДТА соединения $AgAsS_2$ и $Ag_3AsS_3$ выявили два эндотермических эффекта. Эндотермический эффект, наблюдаемый при 695 ± 2 К и 763 ± 2 К, соответствует температуре плавления соединений $AgAsS_2$ и $Ag_3AsS_3$ соответственно. Эндотермический эффект, наблюдаемый при 594 К и 465 К, соответствует полиморфному переходу. По данным СЭМ установлено, что синтезированное соединение имеет нано- и микроразмеры при 413-433 К. Размеры и формы наночастиц и микрочастиц варьируются в зависимости от условий, температуры и pH.

**Ключевые слова:** *органический растворитель, нитрат серебра (I), наночастицы, тиоарсениты, осадок.*