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PREPARATION OF COMPOUND $CuSbS_2$ and Cu_3SbS_3 HYDROTHERMAL METHOD

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(Presented by Academician of ANAS A.M.Aliyev)

The methods of Differential thermal (DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM) analysis investigated the conditions for obtaining with hydrothermal method compounds of $CuSbS_2$ and Cu_3SbS_3 using aqueous solutions of compounds $H[CuCl_2]$ and $KSbO(C_4H_4O_6)\cdot0,5H_2O$. It is found that compounds of nano-sized (40-100 nm) $CuSbS_2$ and Cu_3SbS_3 are obtaining when adding thioacetamide ($CH_3–CS–NH_2$) solution in stoichiometric amounts aqueous solution mixture on rates $H[CuCl_2]$:$KSbO(C_4H_4O_6)\cdot0,5H_2O$=1:1 and $H[CuCl_2]$:$KSbO(C_4H_4O_6)\cdot0,5H_2O$=3:1 mmol at a temperature of 180 ^{0}C. According to the results of DTA it found that nanosized compound $CuSbS_2$ and Cu_3SbS_3 respectively melted at 551 ^{0}C and 605 ^{0}C. The resulting compounds are stable in the range of pH=6-8. When the temperature rising from 40 ^{0}C to 180 ^{0}C yielding compounds and ratio formation of nanoparticles are increases.

***Keywords**: tiostibit, thioacetamide, nanoparticles, makrofoto, yield*

Tiostibits of copper is include list of effective materials used in solar energy converters. Obtaining of these materials are widely using molecular-beam, high-temperature and vacuum methods[1-11].

The most perspectively method of obtaining compounds of $CuSbS_2$ and Cu_3SbS_3 is chemical deposition in aqueous condition. This methods is distinguished by simplicity of devices and regulation of the synthesis conditions. A different na-tured and shaped films are obtaining on the base of the period of chemical deposition from aqueous solution. In the such films are observed better properties. Obtaining many thin films of sulphides ($İn_2S_3$, SnS_2, As_2S_3, Cu_2S etc.) and selenides ($İn_2Se_3$, As_2Se_3, Sb_2Se_3etc.) is applied to with chemical deposition method from aqueous solution[2-8].

From this point of view, one of the most actual matter is obtaining many complex sulphides with chemical deposition method from aqueous solution and study of their properties. Usually, nano-size particles of the substances are formed in obtained thin films with chemical deposition method from aqueous solution. It is known that, many of the physico-chemical properties of nanoparticles differs from the properties of the dense materials[5,6].

Aim at work is explore obtaining conditions compounds of $CuSbS_2$ and Cu_3SbS_3 using from aqueous solution of $H[CuCl_2]$, $KSbO(C_4H_4O_6)\cdot0,5H_2O$ and $CH_3–CS–NH_2$ combinations.

In the article results were given by hydrothermal method synthesis of compounds $CuSbS_2$ and Cu_3SbS_3 using methods RFA, DTA and scanning electron microscopic analysis.

Experimental part and discussion of results

At first component $H[CuCl_2]$ and $KSbO(C_4H_4O_6)\cdot0,5H_2O$ compounds aqueous solutions have been used for synthesize to compounds of $CuSbS_2$ and Cu_3SbS_3. According to composition stoichiometric of compounds $H[CuCl_2]$:$KSbO(C_4H_4O_6)\cdot0,5H_2O$=1:1 and $H[CuCl_2]$: $KSbO(C_4H_4O_6)\cdot0,5H_2O$=3:1 mmol rates was mixtured and added on each mixture in stoichiometric amounts thioacetamide ($CH_3–CS–NH_2$) solution. After stirring the reaction mixture for 15 minutes at 70 ^{0}C was placed in a 100 ml volume autoclaves and thermal processed for 12 hours at 180 ^{0}C. After completion of the reaction sediments filtered through the glass filter, then washed with distilled water at

80 ^{0}C for 1 hour and dried in vacuum. Individuality of acquired compounds have been approved by the RFA (2D PHASER "Bruker", CuK$_\alpha$, 2θ, 20-80 deg.) and DTA (pyrometric HTP-70, device Термоскан-2, inertatmosphere) methods. According to RFA, it was determined that $CuSbS_2$ and Cu_3SbS_3compounds crystallizes in orthorhombic singony. It is observed partially reduction in lattice parameters. The reason for this can be explained that, there are not compensated for the bonds between the atoms in nanoparticles $CuSbS_2$ and Cu_3SbS_3 compounds. Despite this, maximums of intensity matchable peaks at the rentgenograma coincided with the results of other work[5, 11] (Fig.1).

Two endothermic effect is observed at 527 and 521^{0}C in the DTA (pyrometric HTP-70, the device Термоскан-2) curve combination of $CuSbS_2$. At 551^{0}C endothermic effect of the combination is corresponds melting temperature, at 527^{0}C endothermic effect of the combination corresponds to the polymorphic transformation temperature. Endothermic effect observed at 523 and 605^{0}C in the DTA curve combination of Cu_3SbS_3 respectively corresponds polymorphic transformation and melting temperature of compound. As you can see, acquired $CuSbS_2$ and Cu_3SbS_3 compunds temperature of melting and temperature of polymorphic transformation is partially lower than their temperature of monocrystals' melting and temperature of polymorphic transformation. The reason can explained by they have been form nanoparticles.

Elements analysis was conducted (Launch Trion XL dilution refrigerator– OXFORD device) of composition of acquired sediment according to clarify stoichiometric composition of compounds $CuSbS_2$ and Cu_3SbS_3. According to the results, copper, antimony and sulfur weight and the atomic ratios was determined in the compounds contained (Table).

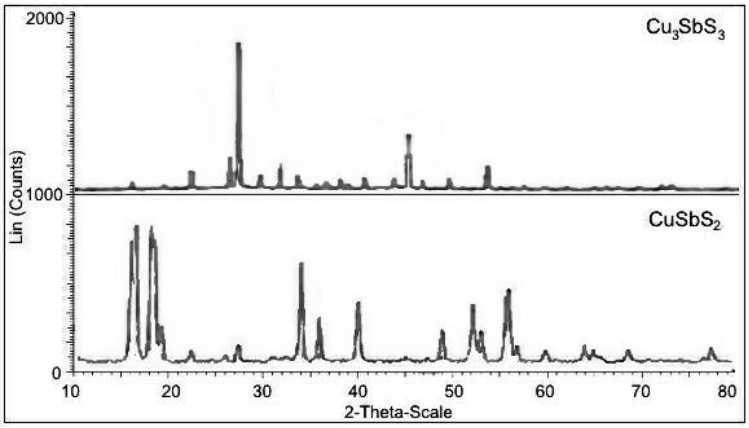

Fig.1. $CuSbS_2$ and Cu_3SbS_3 compounds difraktogram

Table

Result of element analysis of compounds

Compounds	Theamount of elements, %					
	Cu		Sb		S	
	weight	at.	weight	at.	weight	at.
$CuSbS_2$	24,06	23,47	51,24	26,16	24,70	50,37
Cu_3SbS_3	45,74	41,83	30,04	14,42	24,22	43,75

According to the results of the table, it was determined that, the obtained composition stoichiometric of sediments is appropriate of compounds $CuSbS_2$ and Cu_3SbS_3. It was found that, amount of sulphur in the simple formula of compounds is slightly swerve (0,37-0,89 at.%) from stoichiometry. This can be explained by the fact that, when the added to thioacetamide solution to initial mixture certain extent free sulfur is separated because of acidic environment. This is showing themself in synthesis of the compounds.

Micromorphology of obtained compounds $CuSbS_2$ and Cu_3SbS_3 were studied with under a microscope Hitachi TM3000. It was found that, at 180 ^{0}C on the glass base precipitated $CuSbS_2$ and Cu_3SbS_3 compounds were consist of nanoparticles. Nanoparticles' size are range of 40-100 nm. There is not observe amorphous phase in the compounds (Fig. 2). Especially amorphous phase is observed in the synthesized compounds at 40-100 ^{0}C. Combination of $CuSbS_2$ nanoparticles are spherical shape, but Combination of Cu_3SbS_3 nanoparticles are shaped non-spherical high adhesion.

Also effects have been studied condition of pH (pH METER - pH410 "АКВИЛОН") and condition of temperature to yielding of compounds $CuSbS_2$ and Cu_3SbS_3 (Fig. 3). Studied the effect of temperature on yield of compounds $CuSbS_2$ and Cu_3SbS_3 in the range of pH=6-7. It was determined that, yielding of compounds $CuSbS_2$ and Cu_3SbS_3 increasing when the temperature increasing (Fig. 3, a, b).

0,1 M H_2SO_4 and 0,1 M $NH_3{\cdot}H_2O$ solutions were used to study the effects of condition of pH to yielding of compounds $CuSbS_2$ and Cu_3SbS_3. As can be seen from figure 3, the combination of $CuSbS_2$ has maximum yield (94,21-96,63%) in the range of 6÷8 pH (180 ^{0}C). There is observe maximum yield (96,63-97,81%) in the range of 6÷9 pH of combination Cu_3SbS_3. Yielding is decreasing because of compounds broken in the prices of pH<2 and pH>9 (Fig. 3, c, d).

As can be seen from the Figure 3, maximum yield of compounds $CuSbS_2$ and Cu_3SbS_3 are observed intervals of pH=6÷7 and T=120÷180^{0}C. RFA results have shown that, the rate of crystallization of compounds 57.2 and 65.7% was proportionately when thermal processing in autoclave at 180^{0}C for 24 hours aqueous solution of compounds $CuSbS_2$ and Cu_3SbS_3.

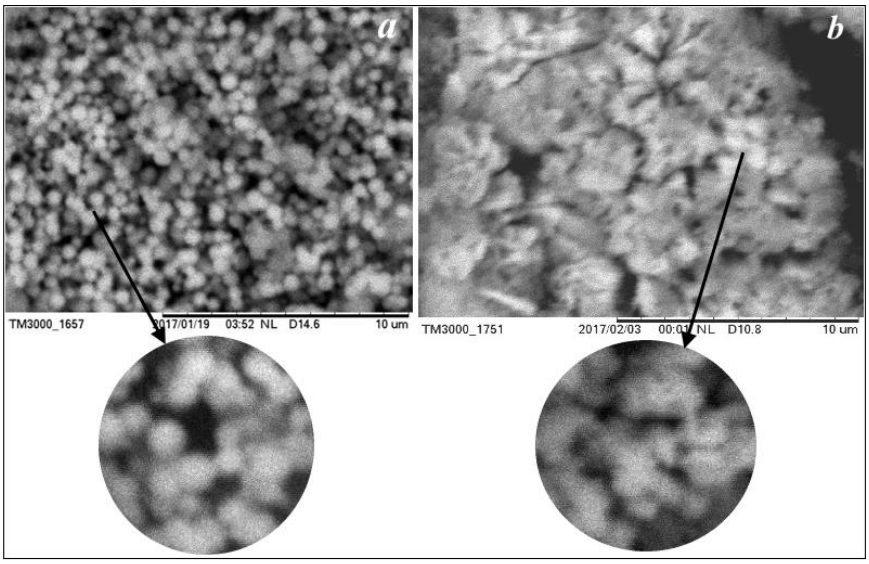

Fig.2. At 180 ^{0}C microphotos of obtained compounds $CuSbS_2$ (a) and Cu_3SbS_3 (b)

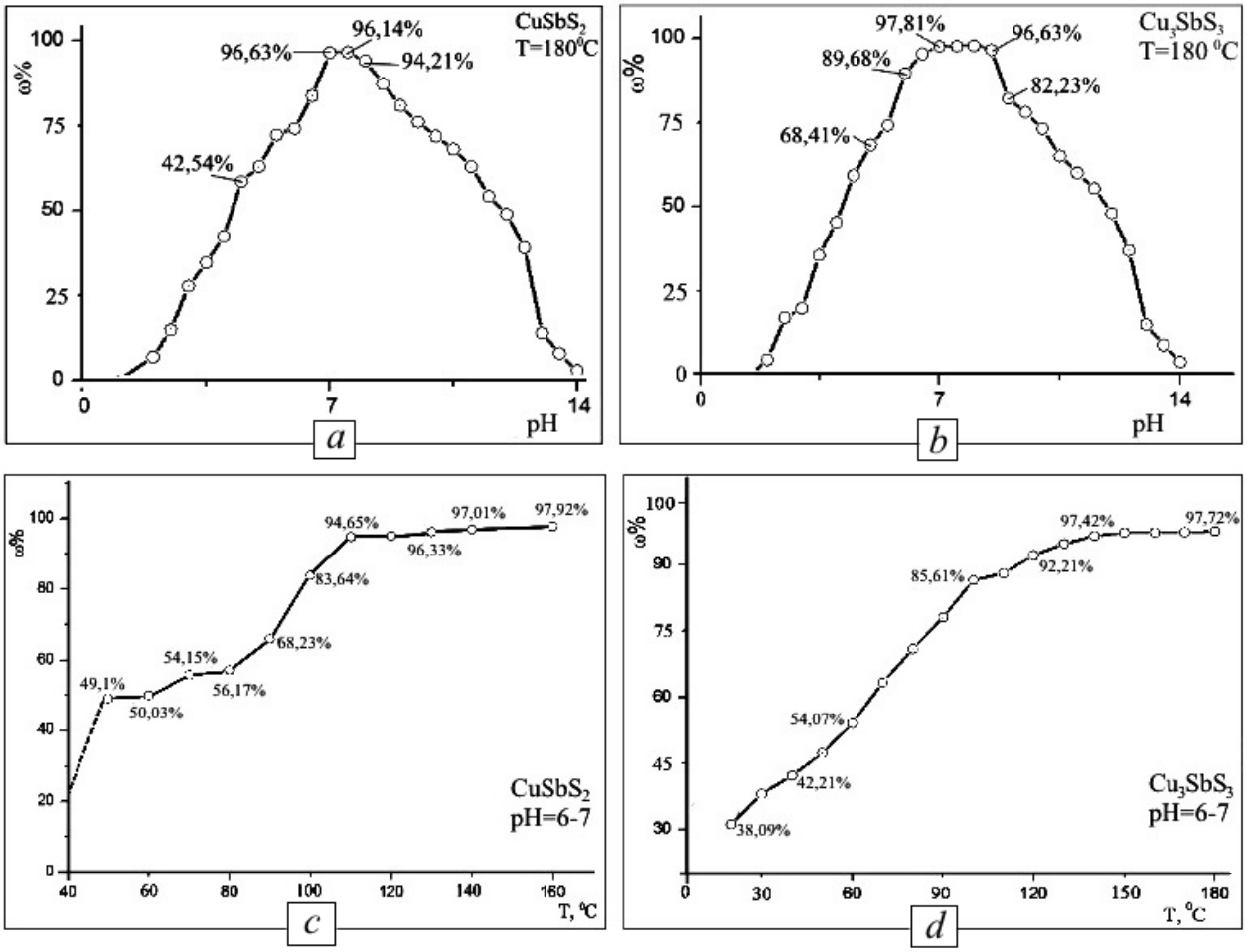

Fig. 3. Dependence from pH condition and temperature yielding of compounds $CuSbS_2$ and Cu_3SbS_3

Result: Synthesized compounds of $CuSbS_2$ and Cu_3SbS_3 and their individuality was approved based on aqueous solutions compounds of $H[CuCl_2]$, $KSbO(C_4H_4O_6)\cdot 0{,}5H_2O$ and $CH_3{-}CS{-}NH_2$. Obtained micromorphology of compounds was studied and it was determined that, at 180 ^{0}C acquired compounds was composed of nanoparticles, their size was range of 40-100 nm. According to the compounds, the range of pH=6÷8 are more durable. The rate of formation of nanoparticles and yielding of compounds are increasing when the increase temperature from 40 ^{0}C to 180 ^{0}C.

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HİDROTERMAL METODLA $CuSbS_2$ və Cu_3SbS_3 BİRLƏŞMƏLƏRİNİN ALINMASI

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Diferensial-termiki (DTA), rentgenfaza (RFA), skanedici elektron mikroskopik (SEM) analiz metodları vasitəsilə $H[CuCl_2]$ və $KSbO(C_4H_4O_6)\cdot 0{,}5H_2O$ birləşmələrinin sulu məhlullarından istifadə etməklə $CuSbS_2$ və Cu_3SbS_3 birləşmələrinin hidrotermal metodla alınması şəraiti tədqiq edilmişdir. Müəyyən edilmişdir ki, 180^0C temperaturda $H[CuCl_2]$: $KSbO(C_4H_4O_6)\cdot 0{,}5H_2O$=1:1 və $H[CuCl_2]$:$KSbO(C_4H_4O_6)\cdot 0{,}5H_2O$=3:1 mmol nisbətlərində qarışığının suda məhlulu üzərinə stexiometrik miqdarda tioasetamid (CH_3–CS–NH_2) məhlulu əlavə etdikdə nanoölçülü (40-100 nm) $CuSbS_2$ və Cu_3SbS_3 birləşmələri alınır. DTA nəticələrinə əsasən, nanoölçülü $CuSbS_2$ və Cu_3SbS_3 birləşmələri müvafiq olaraq 551 və 605^0C-də əriyir. Birləşmələr əsasən, pH=6÷8 aralığında daha davamlıdır. Temperaturu 40^0 C-dən 180^0 C-yə kimi artırdıqda birləşmələrin çıxımı və nanohissəciklərin formalaşma dərəcəsi artır.

***Açar sözlər**: tiostibit, hidrotermal, tioasetamid, nanohissəcik, mikroşəkil, çıxım*

ПОЛУЧЕНИЕ СОЕДИНЕНИЙ $CuSbS_2$ и Cu_3SbS_3 ГИДРОТЕРМАЛЬНЫМ МЕТОДОМ

Г.М.Гусейнов, Н.А.Мамедова, Г.А.Иманов

Дифференциально-термическим (ДТА), рентгенофазовым (РФА), сканирующим электронно-микроскопическим (СЭМ) методами анализа и гидротермальным методом с использованием водных растворов соединений $H[CuCl_2]$ и $KSbO(C_4H_4O_6)\cdot 0{,}5H_2O$ были исследованы условия получения соединений $CuSbS_2$ и Cu_3SbS_3. Установлено, что при добавлении стехиометрического количества тиоацетамида (CH_3–CS–NH_2) к смеси исходных компонентов в мольном соотношении $H[CuCl_2]$:$KSbO(C_4H_4O_6)\cdot 0{,}5H_2O$=1:1 и $H[CuCl_2]$:$KSbO(C_4H_4O_6)\cdot 0{,}5H_2O$=3:1 ммоль, при температуре 180 ^{0}C получаются наноразмерные (40-100 нм) соединения $CuSbS_2$ и Cu_3SbS_3. По результатам ДТА установлено, что наноразмерные соединения $CuSbS_2$ и Cu_3SbS_3 плавятся при 551 и 605 ^{0}C соответственно. Полученные соединения устойчивы в интервале pH=6-8. При поднятии температуры от 40 ^{0}C до 180 ^{0}C выход соединений и коэффициент формирования наночастиц увеличивается.

***Ключевые слова:** тиостибит, тиоацетамид, наночастицы, микрофото, выход*