



Synthesis of Ternary Chalcogenides in Cu-As-Se Systems by the Solvothermal Method in Organic Medium and Production of Nano-and Microparticles

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Abstract: Ternary selenides CuAsSe_2 and Cu_3AsSe_3 were synthesized by the solvothermal method from H [CuCl₂]-As₂Se₃-C₂H₆O₂ system. Nano and microparticles were obtained, and their physical and chemical properties were studied. During syntheses, sodium metaarsenite and copper (I) chloride are mixed in ethylene glycol, and a solution of Na₂SeSO₃ is added as a selenidation reagent according to stoichiometry. These solutions were added to an experimental vessel, placed in a Teflon cuvette, sealed, and placed in a microwave electric heater. The samples are kept in the oven at 413-443 K for 10 hours. After the process, the precipitate is filtered through a glass filter, washed first with dilute hydrochloric acid and distilled water, and finally with ethyl alcohol, and dried in a vacuum at 333-343 K. The productivity of the samples was 90-92 %. Compounds formed at a temperature of 453-473 K dissolve. Nanoparticles of compounds obtained at a temperature of 413-433 K have an irregular shape. Nanoparticles obtained at a temperature of 443 K are in the form of plates. The results of the X-ray phase analysis showed that the compounds correspond to cubic zirconia and belong to the Pm3m spatial structure. Lattice parameters of CuAsSe_2 compound: $a = 5.513 \text{ \AA}$, $Z = 2$ and lattice parameters of Cu_3AsSe_3 compound: $a = 5.76 \text{ \AA}$, $Z = 1$. Based on DTA results, the CuAsSe_2 compound melts congruently at 743 K, while the Cu_3AsSe_3 compound decomposes at 773 K.

Keywords: Solvothermal method, Nanoparticles, Scanning electron microscope, XRF, Melting point, Unit cell

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1. INTRODUCTION

Three-component copper chalcogenides are among the promising functional materials of modern technology. Multicomponent crystalline and amorphous materials of Cu-, Ag-, Ge-, In-, As-, and Sb-based chalcogenides reveal a significant combination of electrical, optical,

magnetic, mechanical, and other physical properties. The study of physical processes in amorphous chalcogenide semiconductor layers has expanded to nanostructures in the recent decade. Despite a wide range of compositions in binary, ternary, and more complex systems of

chalcogenide glasses, the problem of smooth or abrupt modification of parameters still exists. These modifications are performed partially by particular technologies (cooling rate, thin film deposition) or by creating complex artificial structures as known in microelectronic technology. Following the example of microelectronics turning to nanoelectronics on the way to the smaller and more efficient devices exploiting new properties of the crystalline semiconductors at the nano-scale, scientists drew attention to amorphous materials (1-7).

This work demonstrates a simple and elegant strategy for the synthesis of CuInSe_2 with improved control over the chemical composition.

The reaction proceeds via a redox-induced phase transformation of the line compound copper diselenide (CuSe_2) upon incremental addition of elemental indium. Given the chemical and structural similarity between CuSe_2 and CuInSe_2 , stepwise direct transformation of the CuSe_2 structural template into $(1-x)\text{CuSe}_2 / x\text{CuInSe}_2$ nanocomposites without the formation of unwanted binary or ternary indium phases is demonstrated. By X-ray diffraction and transmission electron microscopy, CuInSe_2 particles in size range from 5 to 50 nm of the structural template provided by CuSe_2 are formed (Figure 1) (8).

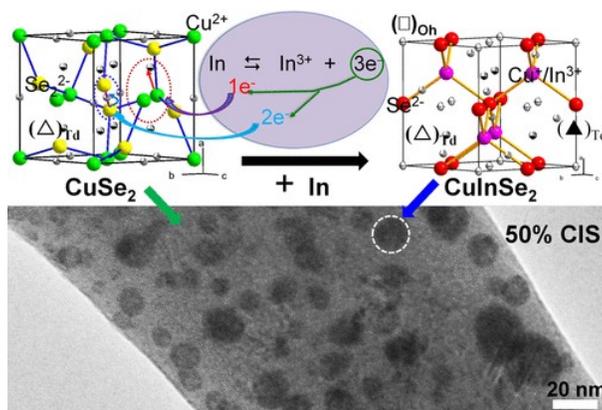


Figure 1: Formed particles of CuInSe_2 in the 5-50 nm size range of the structural template provided by CuSe_2 by X-ray diffraction and transmission electron microscopy.

The $\text{Cu}_5\text{As}_{46.25}\text{Se}_{48.75}$ samples were prepared from arsenic (As) pieces (99.9999 %), selenium (Se) pellets (99.999 + %), and highly enriched copper ^{65}Cu (99.73 % ^{65}Cu and 0.27 % ^{63}Cu) or ^{63}Cu (99.89 % ^{63}Cu and 0.11 % ^{65}Cu) isotopes. The elements were weighed in the correct proportions in a high-purity argon-filled glove box using a balance of precision ± 0.1 mg to give a total sample mass of ≥ 3 g. They were then sealed under vacuum ($\leq 10^{-5}$ torr) in cleaned silica ampoules (5 mm inner diameter and 1 mm wall thickness), heated slowly in a rocking furnace to 870 °C, maintained at this temperature for 6 hours, and finally cooled to 500 °C before quenching in an ice/salt-water mixture. The samples, therefore, are processed in the same fashion to aid materials with identical compositions (9).

($\text{Te}_{85}\text{Se}_{15}$) $_{60-0.6x}\text{As}_{40-0.4x}\text{Cu}_x$ ($x = 0, 10, 16.7, 20, 25$) glasses (TEA1, TEA2, TEA3, TEA4, and TEA5 respectively) were prepared using the melt quenching method. Appropriate amounts of high purity (5N) raw materials Te, Se, As mixed with Cu and sealed in evacuated ($\sim 10^{-3}$ Pa) silica

tubes and melted in a rocking furnace at 1023 K for 10 hours. Then, the glasses were quenched in water and annealed at 5 K lower than their glass transition temperature T_g for 3 hours to relieve internal stresses (10).

The phase diagram $\text{Cu}_2\text{Se}-\text{As}_2\text{Se}_3$ was investigated using thermal and X-ray methods. Cu_2Se has a limited solubility for As_2Se_3 (5 mole % at 769 K). The stoichiometric compound Cu_3AsSe_3 exists between 696 and 769 K. $\text{Cu}_4\text{As}_2\text{Se}_5$, a phase at 66.6 mole % Cu_2Se , decomposes peritectically at 746 K. The narrow homogeneity range (4 mole % at 683 K) extends far into the ternary space. CuAsSe_2 also decomposes peritectically at 683 K. A degenerated eutectic between CuAsSe_2 and As_2Se_3 was found at 641 K. Single crystals of $\text{Cu}_4\text{As}_2\text{Se}_5$ were grown in a salt melt. A metastable modification of the high-temperature phase Cu_3AsSe_3 can be obtained by quenching. $\text{Cu}_4\text{As}_2\text{Se}_5$ (space group $R\bar{3}$, lattice constants $a = 1404.0(1)$ pm, $c = 960.2(1)$ pm), $\text{Cu}_6\text{As}_4\text{Se}_9$, obtained by Cambi and Elli, and $\text{Cu}_7\text{As}_6\text{Se}_{13}$ of Takeuchi and Horiuchi are different versions of a

sphalerite-type compound with a broad homogeneity range in the system Cu-As-Se. CuAsSe₂ is possibly monoclinic with lattice parameters of $a = 946.5(1)$ pm, $b = 1229.3(1)$ pm, $c = 511.7(1)$ pm, and $\beta = 98.546(4)$. The enthalpy of mixing Cu₂Se and As₂Se₃ in the liquid state is endothermic (11).

Analysis of the literature shows that CuAsSe₂ and Cu₃AsSe₃ compounds were obtained from elemental substances only by the bulb synthesis method, with no material about obtaining nano- and microparticles. In our study, the synthesis of glassy ternary chalcogenide semiconductors from the H[CuCl₂]-As₂Se₃-C₂H₆O₂ system containing CuAsSe₂ and Cu₃AsSe₃ by a new, inexpensive method was presented. The influence of the conditions of obtaining nano- and micro-particles of those compounds was studied, and several physicochemical properties were studied.

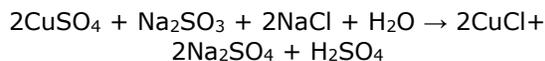
2. EXPERIMENTAL SECTION

2.1. Materials

Ternary copper chalcogenide compounds synthesized from copper (I) chloride and sodium metaarsenite under solvothermal conditions. Sodium selenium sulfate in an ethylene glycol medium is used as a selenizing reagent and the number of reagents taken by stoichiometry.

Preparation of copper (I) chloride and sodium selenosulfate:

Copper (I) chloride is a white tetrahedral crystalline substance that forms salt in the open air and turns blue quickly. CuCl is slightly soluble in water (0.0062 % at 293 K). It is soluble in NH₄OH, hot solid HCl, and chloride solutions of alkali metals. The preparation was obtained according to the following reaction equation using Na₂SO₃ to reduce Cu²⁺ ions from CuSO₄:



250 g of CuSO₄ • 5H₂O and 125 g of NaCl are dissolved and filtered by heating in 900 ml of water. 240 g of Na₂SO₃ dissolved in 530 ml on an aqueous and filtered added to the filtrate heated until a light blue color formed. Separated CuCl is mixed with 40 ml of 2 % hydrochloric acid solution in a bunsen tube and filtered with suction. In this manner, washing continued until the sulfate ions were exhausted. Then, the sediment was washed several times with ethyl alcohol, spread in a thin layer on a porcelain bowl, and dried at 110 °C with occasional stirring (12).

Preparation of sodium selenosulfate from sodium sulfite and elemental selenium. Elemental

selenium reacts with sodium sulfite to form sodium selenosulfate according to the equation: Na₂SO₃ + Se → Na₂SeSO₃. Typically, to prepare a 50 mM solution of Na₂SeSO₃, 0.0987 g of Se powder refluxed with 0.5 g Na₂SO₃ in 20 mL distilled water in a round bottom flask fitted with an air condenser for 3-4 h. An excess concentration of Na₂SO₃ is necessary to prevent the decomposition of Na₂SeSO₃ back into Se and Na₂SO₃. After cooling, the solution was filtered and diluted to 25 mL in a standard measuring flask. This solution is used immediately for the synthesis (13, 14).

2.2. The Method of Obtaining CuAsSe₂

First, the stoichiometry, sodium metaarsenite and copper (I) chloride are mixed in 20 ml of ethylene glycol, and then the selenizing agent sodium selenosulfate (pH = 7-5) is added. The mixture is heated in a sealed glass ampoule in an electric microwave oven (Speedwave four BERGHOF - Germany). The sample was kept in a heater between 413 and 443 K for 6 hours. The resulting precipitate is filtered through a glass filter, washed with the dilute hydrochloric acid solution, ultrapure water, and ethyl alcohol, and dried in a vacuum at 333-343 K.

2.3. Synthesis method of Cu₃AsSe₃

The composition is synthesized from CuCl, NaAsO₂, and sodium selenosulfate under solvothermal conditions. The mixture is stirred in 20 ml of ethylene glycol sodium selenosulfate (pH = 7-5) and heated in a sealed glass bulb in an electric microwave oven. The sample is kept in a heater at a temperature of 413-443 K for 6 hours.

The yield of both substances is 90-92 %. At a temperature (453-473 K), the resulting precipitate of CuAsSe₂ and Cu₃AsSe₃ partially dissolves in a solution (ethylene glycol). The composition of the obtained compound (Cu-As-Se ratio) was determined in a NETZSCH STA 449F349F3 (Germany) thermal analyzer and chemical analysis. Differential thermal analysis (DTA) was carried out with an HTP-70 pyrometer, Thermoscan-2 unit, in an inert atmosphere. The phase analysis of CuAsSe₂ and Cu₃AsSe₃ nano- and microparticles was studied using a Bruker D8 ADVANCE X-ray diffractometer (CuKα, λ = 1.5406 Å, 0 < 2θ < 80°). Morphological studies were performed using scanning electron microscopy TM3000 (Hitachi, Japan).

3. RESULTS AND DISCUSSION

3.1. TG Analysis

It is known that, depending on the conditions of acquisition, chalcogenides in the organic or aqueous mediums of various synthesized compositions CuAsSe_2 , Cu_3AsSe_3 , $\text{Cu}_4\text{As}_2\text{Se}_5$,

$\text{Cu}_8\text{As}_2\text{Se}_7$ etc. with different stoichiometry. Therefore, thermogravimetric analysis was carried out using the hydrothermal method in the NETZSCH STA 449F349F3 instrument. The results of the reacher are shown in Figure 2.

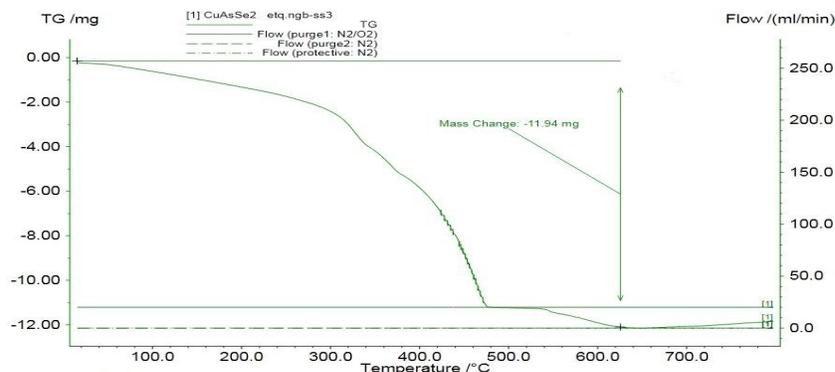


Figure 2: TGA diagrams of CuAsSe_2 .

They were within 20 - 800 °C, and the air supply rate was 40 ml/min. Weight loss at a temperature of 20 - 625 °C is 11.94 mg. A sample weighing 14.95 mg was taken for analysis. The theoretically contains 3.78 mg of arsenic and 7.95 mg of selenium (total 3.78 + 7.95 = 11.73 mg). The weight loss (11.94 mg in the experiment) occurred due to As and Se, and

this number is consistent with the theoretically calculated amounts. The remainder (3.01 mg) coincides with the theoretically calculated amount of copper (3.12 mg). All this shows that the formula for the CuAsSe_2 compound is correct. The thermal differential analysis of the CuAsSe_2 alloy indicated congruent melting at 480 °C.

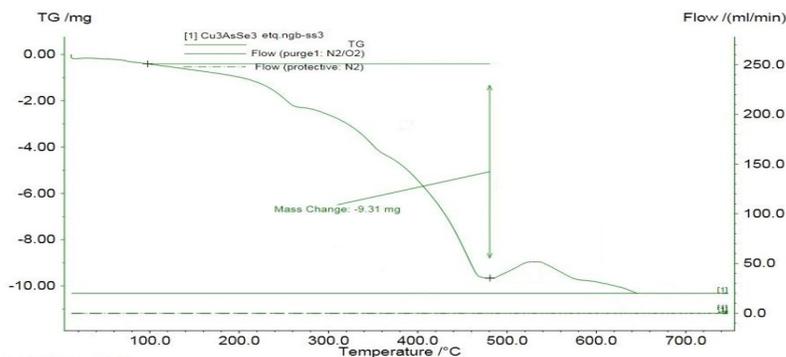


Figure 3: TGA diagrams of Cu_3AsSe_3 .

The heating of the samples was carried out within the temperature range of 20 - 750 °C. A sample weighing 15 mg was taken for analysis. In the Cu_3AsSe_3 sample at a temperature of 20-480 °C, the weight loss is 9.31 mg (Figure 3), which corresponds to the theoretically calculated amount of arsenic and selenium (2.23 mg As + 7.05 mg Se = 9.28 mg). The remaining 5.69 mg corresponds to the content of copper (5.71 mg) in the sample. The results obtained confirm the

correctness of the formula for the compound Cu_3AsSe_3 .

Endo effects observed at 220 °C, 480 °C, 560 °C in TGA of Cu_3AsSe_3 compound. The thermal effect at 220 °C corresponds to the decomposition of Cu_3AsSe_3 into CuAsSe_2 , the effect at 480 °C corresponds to the oxidation of Cu_2O , and the effect at 560 °C corresponds to the oxidation of Cu_2O to CuO .

According to the DTA results, the CuAsSe_2 compound melts congruently at 470°C , and the Cu_3AsSe_3 compound melts with decomposition at 500°C .

3.2. X-Ray Structure Determination

X-ray phase analysis of the compound CuAsSe_2 and Cu_3AsSe_3 studied patterns showed that the CuAsSe_2 and Cu_3AsSe_3 compounds crystallize into the cubic crystal system (CuAsSe_2 sp. gr.: $a = 5.513 \text{ \AA}$), Cu_3AsSe_3 (sp. gr.: $a = 5.758 \text{ \AA}$) (Figure 4, 5).

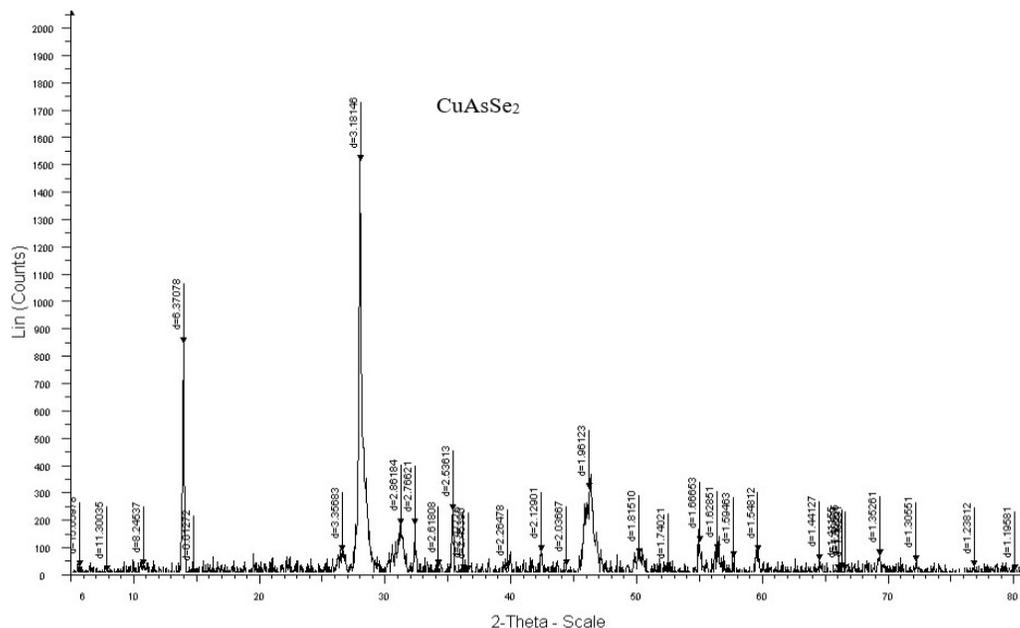


Figure 4: X-ray diffraction pattern of CuAsSe_2 .

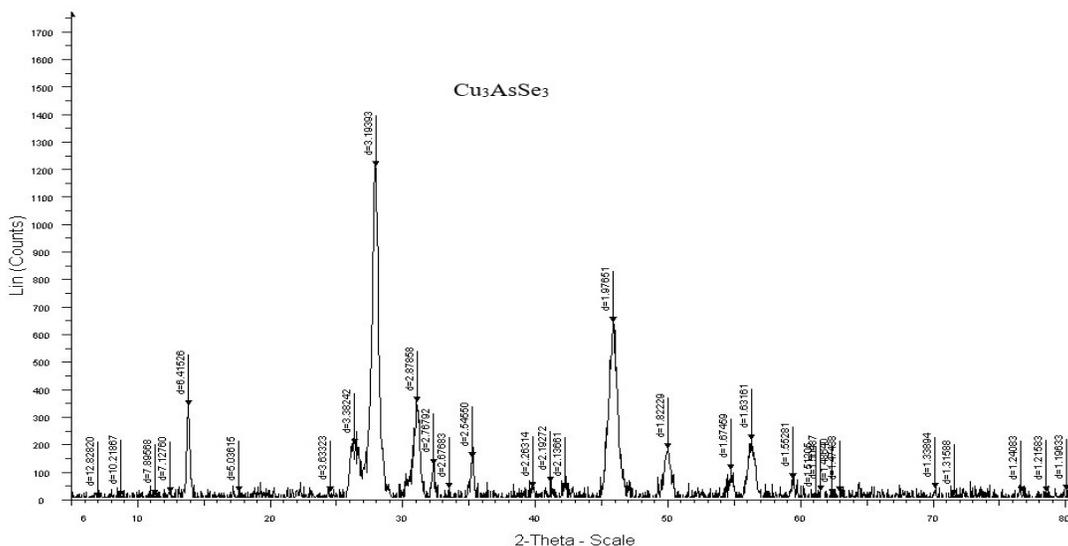


Figure 5: X-ray diffraction pattern of Cu_3AsSe_3 .

X-ray diffraction pattern of arsenic copper selenide (CuAsSe_2 , Cu_3AsSe_3) intensity and position of the developing peaks fully comply with the standards (PDF 00-012-0379).

3.3. SEM analysis

The effect of temperature growth and formation of nano and microparticles synthesized by the solvothermal method was studied, and the sizes of these particles were taken in an electron

microscope (Figure 6, 7). As the temperature changes from 413 K to 443 K, they gradually transform into different formations. It can be seen from the picture that the CuAsSe_2 and

Cu_3AsSe_3 nanoparticles obtained at the temperature of 413 K have an irregular shape (Figure 6 a, b).

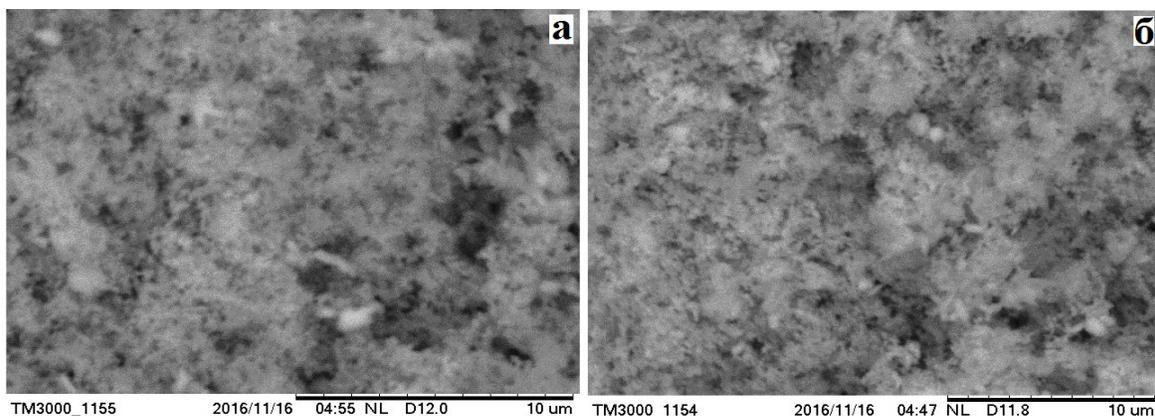


Figure 6: SEM photographs of CuAsSe_2 (a) and Cu_3AsSe_3 (b) nanoparticles at 413 K.

Furthermore, at a temperature of 443 K, formed nano and microplates (Figure 7 a, b). nanoparticles (CuAsSe_2 and Cu_3AsSe_3) are

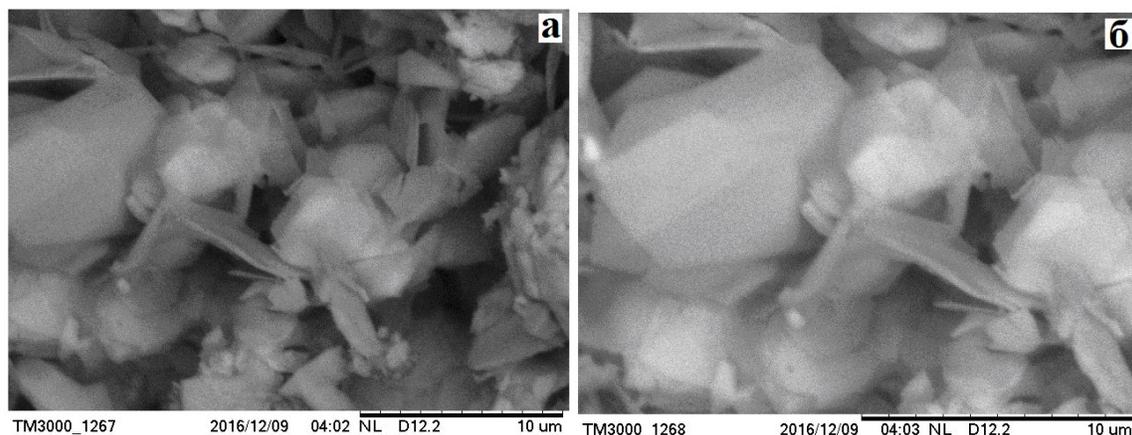


Figure 7: SEM photographs of CuAsSe_2 (a) and Cu_3AsSe_3 (b) nanoparticles at 443 K.

It was determined that the formation of nano- and microparticles depends on temperature and time in the liquid phase. Thus, when As^{3+} and Se^{2-} interact in an ethylene glycol medium, a dark brown precipitate (pH=10) is formed. After heating for 10 hours, a coagulated black settled in the reaction vessel.

3.4. Thermal Properties

The DTA thermograms show that one endothermic peak was observed on the curves (Figure 8 a, b).

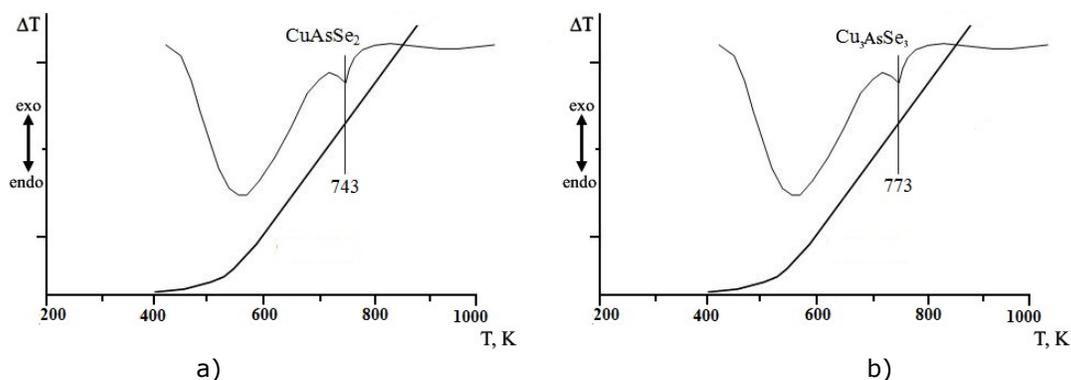


Figure 8: DTA curves of CuAsSe_2 (a) and Cu_3AsSe_3 (b) samples.

The melting temperature of CuAsSe_2 is (endotherm point) 743 K, and the melting point of Cu_3AsSe_3 is 773 K. When examined by differential thermal analysis, the CuAsSe_2 compound melts congruently at 743 K, the Cu_3AsSe_3 compound decomposes at 773 K melts.

3.5. Chemical Analysis

Chemical analysis of the samples (CuAsSe_2 , Cu_3AsSe_3) was performed in an atomic absorption spectrophotometer (The Thermo Scientific AA Spectrometer ICE 3500 - a True Dual Atomizer AAS). **COPPER**, 1000 mg/L. A minimum of 1.000 g of copper metal was dissolved in (1+1) HNO_3 . Dilute to 1 liter with 1 % (v/v) HNO_3 . **ARSENIC**, 1000 mg/L. 1.320 g of arsenic oxide (As_2O_3) was dissolved in 25 mL of 20 % (w/v) KOH solution. Neutralize with 20 % (v/v) H_2SO_4 to the

phenolphthalein endpoint. Dilute to 1 liter with 1 % (v/v) H_2SO_4 . **SELENIUM**, 1000 mg/L. Dissolve 1.000 g of selenium metal in a minimum volume of concentrated HNO_3 . Evaporate to dryness, add 2 mL of water, and evaporate to dryness 2 or 3 more times. Dissolve in 10 % (v/v) HCl and dilute to 1 liter with 10 % (v/v) HCl (15).

A sample weighing 0.1-2.0 g was placed in an Erlenmeyer flask, and a certain amount of concentrated HNO_3 acid was added and kept in a mechanical shaker for about 15 minutes. The sample is then heated at the selected temperature for 30 minutes to several hours, filtered through a glass filter with deionized water or dilute acid solution, filtered into a 50 ml volumetric flask, and diluted again to 50 ml. The data results are shown in Table 1.

Table 1. Results of chemical analysis of the compound CuAsSe_2 and Cu_3AsSe_3 .

Sample, g	Number of elements, g					
	Cu		As		Se	
	Theor.	Pract.	Theor.	Pract.	Theor.	Pract.
CuAsSe_2 , 0.1482	0.0319	0.0315	0.0374	0.0369	0.0788	0.0781
Cu_3AsSe_3 , 0.1467	0.0559	0.0552	0.0218	0.0213	0.0388	0.0380

As can be seen from the data in the table, the chemical analysis of the compounds also confirms the formula of the compounds - CuAsSe_2 and Cu_3AsSe_3 .

4. CONCLUSION

The simple synthesis methods were developed for ternary copper chalcogenides in an ethylene glycol medium without polluting the environment. CuAsSe_2 and Cu_3AsSe_3 compounds were synthesized from copper (I) chloride, sodium metaarsenite, and sodium selenosulfate. These

compounds (nanoparticles) were obtained in the temperature range of 413-443 K for 10 hours (pH = 7-5). 90-92 % of the results were obtained. Nanoparticles of compounds obtained at a temperature of 413-433 K have an irregular shape. Nanoparticles obtained at a temperature of 443 K are in the form of plates. SEM analysis of compounds was not found in the literature, so it is possible to look for the first time in our research. X-ray phase analysis was performed, and it was determined that the compounds correspond to cubic syconia and belong to the Pm3m spatial structure position of the developing

peaks is consistent (PDF 00-012-0379) (11). According to the DTA results, the CuAsSe_2 compound congruently at 743 K, and the Cu_3AsSe_3 compound decomposes at 773 K melts. The stoichiometric compound Cu_3AsSe_3 exists between 696 and 769 K. CuAsSe_2 was also peritectic at 683 K, and eutectic composition between CuAsSe_2 and As_2Se_3 was found at 641 K (11). Thermogravimetric analysis was performed. The thermal differential of the CuAsSe_2 alloy showed congruent melting at 753 K. Endo effects were observed at 493 K, 753 K, and 833 K in the TGA of the Cu_3AsSe_3 compound. Thermal differential analysis at 493 K corresponds to the decomposition of Cu_3AsSe_3 to CuAsSe_2 , 753 K to the oxidation of Cu_2O , and 833 K to the oxidation of Cu_2O to CuO .

Among copper metal-doped chalcogenide glasses, ternary selenides attracting more attention for their potential applications in semiconductor technology, nano- and microelectronics. Therefore, the development of the technology of semiconductor devices and the expansion of the class of combinations with parameters, which allows controlling their physical properties, is envisaged.

5. ACKNOWLEDGMENTS

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