

Production of Nanoparticles of AgAsSe_2 and Ag_3AsSe_3 Compounds

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Abstract: Ternary compounds (nano- and microparticles) of AgAsSe_2 and Ag_3AsSe_3 have been synthesized from approximately equimolar mixtures of silver nitrate, sodium metaarsenite and sodium selenosulfate with prepared by refluxing selenium powder with concentrated sodium sulfite solution under hydrothermal conditions in ethylene glycol medium. The solutions were put into a 100 mL Teflon-lined stainless steel autoclave Speedwave four BERGHOF and sealed and then heated at the temperature of 443 K during 8 hours ($\text{pH} = 5-4$). The products were filtered via the glass filter and washed by deionized water and absolute ethanol for several times, then dried at 353 K in a vacuum oven for at least 1 hour for analysis. The thermogravimetric (TG) and electron microprobe analysis have been carried out. The results showed that the composition of silver selenoarsenate compounds corresponded to the formulas AgAsSe_2 and Ag_3AsSe_3 . The results of SEM images and shows the typical morphologies of synthesized products in which tubular- and stick-shaped like nano-particles can be observed and their size can be estimated from 140 nm to 310 nm. The compound of AgAsSe_2 and Ag_3AsSe_3 was constructed using X-ray phase and differential-thermal analyses. It is ascertained by X-ray powder diffraction (XRD) that the parameters of AgAsSe_2 crystallized in the tetragonal space group $R3m$ with $a = 12.54 \text{ \AA}$, $c = 11.14 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $Z = 5$, Ag_3AsSe_3 (this compound is an allotrope of $\beta - \text{Ag}_3\text{AsSe}_3$) crystallizes in the orthorhombic space group $Pnma$, $a = 8.11 \text{ \AA}$, $b = 11.34 \text{ \AA}$, $c = 20.73 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $Z = 8$. The results of differential thermal analysis (DTA) AgAsSe_2 compound melts congruently at $T_g = 683 \text{ K}$, Ag_3AsSe_3 with incongruent type of melting at $T_g = 663 \text{ K}$ was established.

Keywords: Hydrothermal synthesis; organic solvent; arsenic(III) selenide; XRD; scanning electron microscopy.

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INTRODUCTION

Chalcogenide glasses are very promising materials for use in fiber optics and integrated optics since they have many unique optical properties and exhibit a good transparency in the infrared region (1). The quasi-binary $\text{Ag}_2\text{Se}-\text{As}_2\text{Se}_3$ system is interesting due to the formation of the semiconductor Ag_3AsSe_3 and the compound AgAsSe_2 (2). Since the sulfur analogs of these compounds are natural minerals with interesting optical properties, the investigation of the compounds in the Ag-As-Se system is an important step in the search for new materials for optoelectronics (3). The polythermal section of the $\text{Ag}_2\text{Se} - \text{As}_2\text{Se}_3$ system was proposed for the first time. It was found that the system is quasibinary. In addition the formation of two ternary compounds at the compositions Ag_3AsSe_3 and AgAsSe_2 was established. The Ag_3AsSe_3 compound forms according to a peritectic reaction at 673 K, whereas the AgAsSe_2 compound melts congruently at 683 K. The possibility of a polymorphic transformation of AgAsSe_2 at 658 K was also suggested in (4). The crystal structure of the Ag_3AsSe_3 compound (space group $R3c$; $a = 1.1298$ nm, $c = 0.8757$ nm) was determined in (5). The crystal structure of the high-temperature modification of AgAsSe_2 (space group $R3m$; $a = 0.3915$ nm, $c = 2.0375$ nm) was reported. The X-ray powder diffraction pattern of the low temperature modification of AgAsSe_2 was indexed in a tetragonal unit cell ($a = 1.2548$ nm, $c = 1.1140$ nm) (6). New results of investigations of the AgAsSe_2 compound were reported in (7). 14 samples were prepared for the investigation of the phase diagram of the $\text{Ag}_2\text{Se} - \text{As}_2\text{Se}_3$ system. The alloys were prepared by sintering the elemental constituents of purity better than 99.999 wt% in an evacuated quartz ampoule. The synthesis was carried out in a tube resistance furnace. The ampoules were first heated with a rate of 25 K per hour up to 1200 K and then kept at this temperature for 5 hours. Afterwards the samples were slowly cooled (5 K per hour) down to 520 K and annealed at this temperature for 600 hours. Subsequently the ampoules were quenched in cold water. The results of their investigation of the $\text{Ag}_2\text{Se}-\text{As}_2\text{Se}_3$ system are shown that, the formation of three compounds, Ag_3AsSe_3 , AgAsSe_2 , and AgAs_3Se_5 was confirmed (8). The temperatures of the non-variant processes are similar to those reported in (9). However, a polymorphic transformation of AgAsSe_2 at 658 K was observed. A similar arrangement of Ag- and As-centered octahedron is observed in the structure of AgAsSe_2 (space group $R3m$, $a = 0.3915$ nm, $c = 2.037$ nm) (6) (Figure 1). The Se atoms in the structure of AgAsSe_2 are also stacked in a close-packed arrangement with the layers in the sequence ABC but all the octahedral interstices are occupied. The Ag atoms occupy half of the octahedral interstices, and the As atoms are located in the remaining ones (8).

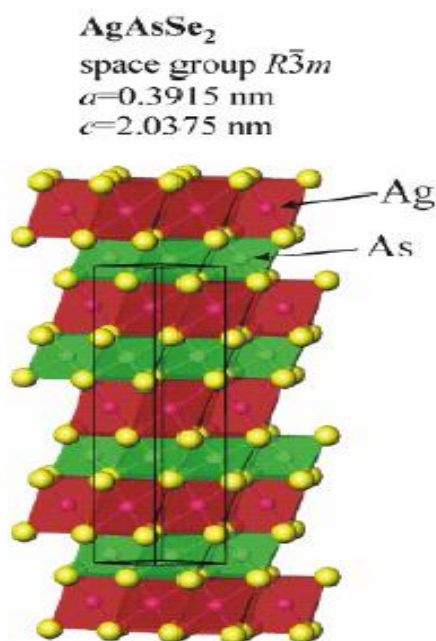


Figure 1: Stacking of Ag- and As-centered octahedra in the structures of the AgAsSe_2 compound.

An interesting set of anionic species which can serve as building units to construct complex multinary solids is that of thioarsenates and thioantimonates $[\text{Pn}_x\text{Q}_y]^{n-}$, ($\text{Pn} = \text{As}, \text{Sb}$; $\text{Q} = \text{S}, \text{Se}$). Several compounds based on these anions have been prepared. The majority of them involve ternary systems associated with alkali metals and organic counter-ions (10). Three new solid state silver selenoarsenates and one thioarsenate prepared from hydro- and methanothermal synthesis are described. β - Ag_3AsSe_3 (I) and $(\text{Me}_3\text{NH})[\text{Ag}_3\text{As}_2\text{Se}_5]$ (II) were synthesized hydrothermally at $110 \text{ }^\circ\text{C}$ from a mixture of $\text{AgBF}_4 / 3\text{K}_3\text{AsSe}_3$ and $\text{AgBF}_4 / 3\text{K}_3\text{AsSe}_3 / 6\text{Me}_3\text{NHCl}$, while $\text{K}_5[\text{Ag}_2\text{As}_3\text{Se}_9]$ (III) and $\text{K}[\text{Ag}_3\text{As}_2\text{Se}_5]$ (IV) were synthesized methanothermally at $110 \text{ }^\circ\text{C}$ from a mixture of $\text{AgBF}_4 / 3\text{K}_3\text{AsS}_3$ and $\text{AgBF}_4 / 3\text{K}_3\text{AsSe}_3$ respectively. β - Ag_3AsSe_3 (I) crystallizes in the orthorhombic space group Pnma (No. 62) with $a = 8.111(1) \text{ \AA}$, $b = 11.344(2) \text{ \AA}$, $c = 20.728(3) \text{ \AA}$, $Z = 8$, $V = 1907(1) \text{ \AA}^3$. This compound is a new allotrope of α - Ag_3AsSe_3 and has a complex three-dimensional structure composed of distorted trigonal planar and tetrahedral Ag^+ ions and $[\text{AsSe}_3]^{3-}$ units. $(\text{Me}_3\text{NH})[\text{Ag}_3\text{As}_2\text{Se}_5]$ (II) crystallized in the triclinic space group $\text{P}-1$ (No. 2) with $a = 10.119(2) \text{ \AA}$, $b = 18.010 \text{ \AA}$, $c = 14.932(3) \text{ \AA}$, $\alpha = 110.20(1)^\circ$, $\beta = 103.98(2)^\circ$, $\gamma = 99.99(1)^\circ$, $Z = 2$, $V = 729.3(3) \text{ \AA}^3$. The $[\text{Ag}_3\text{As}_2\text{Se}_5]_n^{n-}$ anion in (II) has a complex two-dimensional layered structure with tetrahedral Ag^+ ions and $[\text{As}_2\text{Se}_5]^{4-}$ units. $\text{K}_5[\text{Ag}_2\text{As}_3\text{Se}_9]$ (III) crystallizes in the orthorhombic space group Pnma (No. 62) with $a = 12.599(2) \text{ \AA}$, $b = 12.607(4) \text{ \AA}$, $c = 14.067(3) \text{ \AA}$, $Z = 8$, $V = 2234(1) \text{ \AA}^3$. The $[\text{Ag}_2\text{As}_3\text{Se}_9]_n^{5n-}$ anion in (III) has a two-dimensional layered structure with tetrahedral Ag^+ ions and two different kinds of selenoarsenate units, $[\text{AsSe}_4]^{3-}$ and $[\text{As}_2\text{Se}_5]^{4-}$. $\text{K}[\text{Ag}_3\text{As}_2\text{Se}_5]$ (IV) also crystallizes in the orthorhombic space group Pnma (No. 62) with $a = 19.210(2) \text{ \AA}$, $b = 18.867(2) \text{ \AA}$, $c = 6.3491(7) \text{ \AA}$, $Z = 8$, $V = 2057.2(7) \text{ \AA}^3$. The $[\text{Ag}_2\text{As}_3\text{S}_5]_n^{n-}$ anion in (IV) possesses a complicated two-dimensional structure with tetrahedral Ag^+ ions and two kinds of thioarsenate

ligands, $[\text{AsS}_3]^{3-}$ and $[\text{As}_3\text{S}_7]^{5-}$ (11). It is 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 selenoarsenates in ethylene glycol medium is almost absent in the literature. Taking this into account, in the synthesis of, AgAsSe_2 and Ag_3AsSe_3 compounds we used ethylene glycol as the solvent.

In this article we report the mechanism of synthesis and results of AgAsSe_2 and Ag_3AsSe_3 compounds nano- and microparticles obtaining conditions in ethylene glycol medium and observed results.

MATERIALS AND METHODS

The samples of AgAsSe_2 and Ag_3AsSe_3 were prepared for the investigation of the interaction between the components in the $\text{AgNO}_3 - \text{NaAsO}_2 - \text{Na}_2\text{SeSO}_3$ system in ethylene glycolic medium under hydrothermal conditions. In a typical synthesis of AgAsSe_2 and Ag_3AsSe_3 nano- and microparticles, were taken in molar ratio purity better than 99.999 wt. % AgNO_3 and NaAsO_2 were dissolved in 30 mL of ethylene glycol. The pH of the solution is adjusted to 5-4 and appropriate stoichiometry of 0.1 M Se (Na_2SeSO_3) is added with continuous stirring. The solutions were put into a 100 mL Teflon-lined stainless steel autoclave Speedwave four BERGHOF and sealed and then heated at 443 K for 8 h. After that, the autoclave was cooled to room temperature naturally. The products were filtered via the glass filter and washed by deionized water and absolute ethanol for several times, then dried at 353 K in vacuum oven for at least 1 hour for analysis.

Na_2SeSO_3 is prepared by refluxing Se metal powder with concentrated Na_2SO_3 solution. Typically, to prepare a 50 mM solution of Na_2SeSO_3 , 0.0987 g of Se powder is refluxed with 0.5 g Na_2SO_3 in 20 mL distilled water in a round bottom flask fitted with an air condenser for 3-4 h. An excess concentration of Na_2SO_3 is necessary to prevent the decomposition of Na_2SeSO_3 back into Se and Na_2SO_3 . After cooling down, the solution is filtered and diluted to 25 mL in a standard measuring flask. This solution should be used immediately for the synthesis (12).

The substances thus obtained was investigated using a morphology, X-ray powder diffraction, thermogravimetric analysis, electron microprobe analysis and differential thermal analysis.

RESULTS AND DISCUSSION

SEM analysis

The morphological characteristics of as-synthesized products were investigated by scanning electron microscopy (SEM, Hitachi-TM3000). AgAsSe_2 and Ag_3AsSe_3 nano- and micro-particles

synthesized in ethylene glycol with 8 hours at 443 K. Upon increasing the temperature, they gradually transformed into different morphologies. The results of SEM image and shows the typical morphologies of synthesized products in which tubular and stick shaped like nanoparticles can be observed and their size can be estimated from 140 nm to 310 nm (Figure 2).

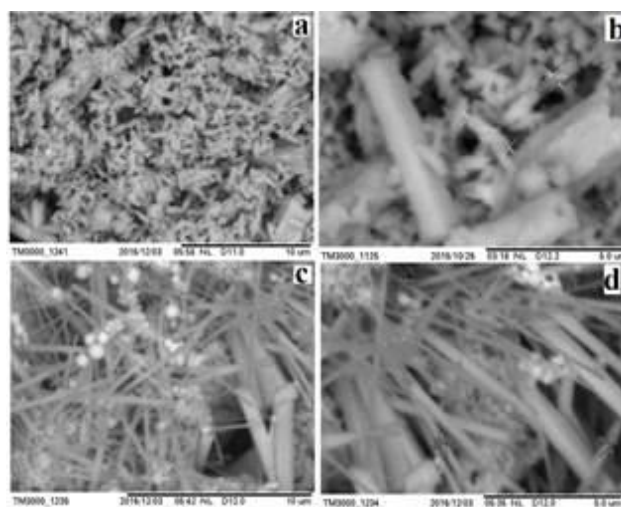


Figure 2: SEM photographs of nano- and microparticles of AgAsSe_2 (a, b) and Ag_3AsSe_3 (c, d) compounds at 443 K.

X-Ray Structure Determination

The crystal structures of as-synthesized products were characterized by X-ray powder diffraction (XRD, Bruker D8 ADVANCE, $\text{CuK}\alpha$, $\lambda = 1.5406 \text{ \AA}$, $0 < 2\theta < 80^\circ$) and determination was performed using the FWHM (full width at half maximum) evaluation program. Figure 3 shows the XRD pattern of as synthesized products, in which Ag_3AsSe_3 diffraction peaks can be indexed as the structured β - Ag_3AsSe_3 with the lattice parameter (Standard Identification Card, (C) 01-086-1540) in Table 1. Our experimental XRD patterns agree with those calculated issuing from the structural data reported in the literature.

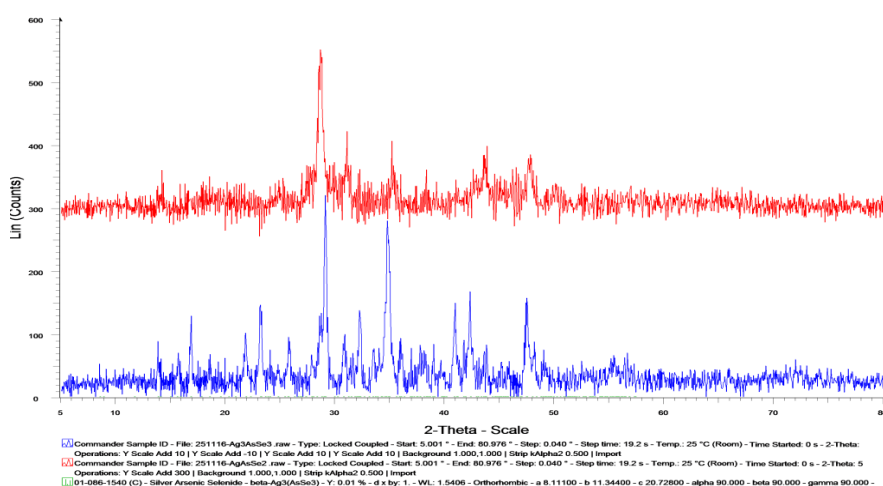


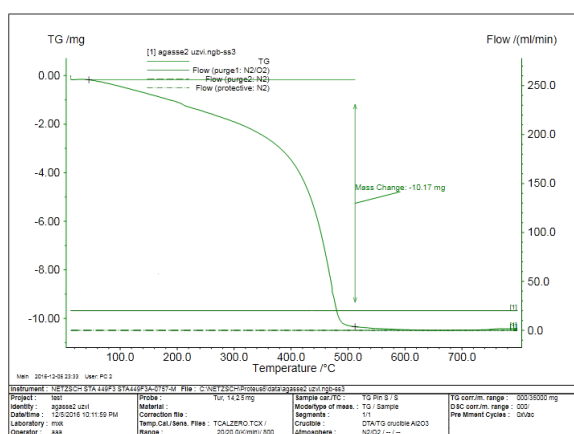
Figure 3: XRD of AgAsSe_2 and Ag_3AsSe_3

Table 1. Results of the crystal structure determination of the AgAsSe_2 and Ag_3AsSe_3 compounds

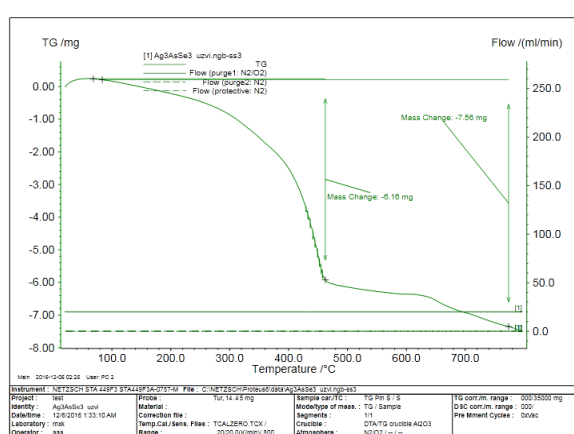
Empirical formula	Crystal structure, Space group	Lattice parameters				Number of formula units per unit cell
		$a, \text{Å}$	$b, \text{Å}$	$c, \text{Å}$	a, β, γ	
AgAsSe_2	tetragonal, R3m	12.54	-	11.14	$\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$	$Z = 5$
Ag_3AsSe_3 , β - Ag_3AsSe_3	orthorhombic, Pnma	8.11	11.34	20.73	$\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$	$Z = 8$

TG analysis

The thermogravimetric analysis of the produced AgAsSe_2 and Ag_3AsSe_3 compounds stoichiometric composition is carried out in the presence of air by the derivatograph NETZSCH STA 449F3. The results are shown in the Figures 4a, and b. According to TGA data the sample is heated between at 293-1073 K temperature. The weather giving out of the rate of 40 mL/s has been. Figure 3a shows that the mass loss is 10.17 mg at 293-793 K temperature. It is the theoretical mass of silver (4.51 mg), arsenic (3.13 mg), selenium (6.60 mg) on the sample of 14.25 mg. So, weight loss is consistent with the quantity of arsenic and selenium (3.13 mg As + 6.60 mg Se = 9.73 mg). Ag_3AsSe_3 sample heated to 1073 K temperature (Figure 4b). At this time the weight loss (1053 K) was 7.56 mg. The weight loss corresponds to the evaporation of arsenic and selenium (1.70 mg As + 5.38 mg Se = 7.08 mg). It is seen that our calculations, the residue mass (6.89 mg) is appropriate with the price theoretical calculated (7.36 mg). From here silver remains in the residue. The size of the weight loss steps observed in the TGA diagrams are in agreement with the theoretical values.



a)



b)

Figure 4: TGA diagrams of AgAsSe_2 (a) and Ag_3AsSe_3 (b).

Electron microprobe analysis

The elementary analysis of the compound composition is made by the method of electron microprobe analysis (on the device Launch Trion XL dilution refrigerator-OXFORD). The results are shown in the following table 2.

Table 2. The elementary analysis results of AgAsSe₂ and Ag₃AsSe₃ compounds.

Elements	AgAsSe ₂		Ag ₃ AsSe ₃	
	Weight, %	Atomic, %	Weight, %	Atomic, %
Ag	31.65	24.73	50.93	42.73
As	21.96	24.97	11.74	14.55
Se	46.32	50.3	37.33	42.72
Totals	100.0	100.0	100.0	100.0

Thermal Properties

The thermal behavior of AgAsSe₂ and Ag₃AsSe₃ were investigated with differential thermal analysis (Thermoscan-2 unit, inert atmosphere) Figures 5a, and b. The DTA thermogram shows that one endothermic peak was observed in the curves. The compound AgAsSe₂ melting point endotherm, at $T_g = 683$ K, and Ag₃AsSe₃ point endotherm with incongruent type of melting at $T_g = 663$ K.

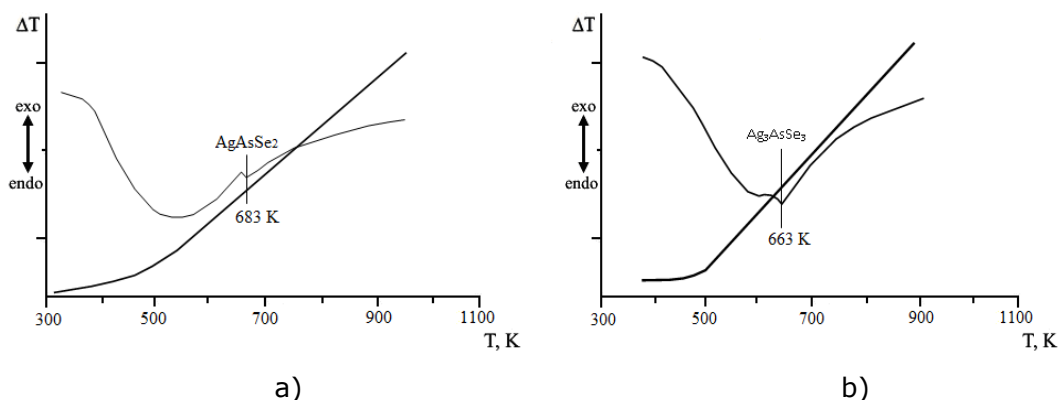


Figure 5. DTA data for AgAsSe₂ (a) and Ag₃AsSe₃ (b)

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