# Accepted Manuscript

Thermal stability of nanoparticle size and phase composition of nanostructured  $Ag_2S$  silver sulfide

Stanislav I. Sadovnikov, Emma G. Vovkotrub

PII: S0925-8388(18)32472-1

DOI: 10.1016/j.jallcom.2018.06.351

Reference: JALCOM 46687

To appear in: Journal of Alloys and Compounds

Received Date: 8 February 2018

Revised Date: 22 June 2018

Accepted Date: 28 June 2018

Please cite this article as: S.I. Sadovnikov, E.G. Vovkotrub, Thermal stability of nanoparticle size and phase composition of nanostructured Ag<sub>2</sub>S silver sulfide, *Journal of Alloys and Compounds* (2018), doi: 10.1016/j.jallcom.2018.06.351.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.





Cithe Marine

# Thermal Stability of Nanoparticle Size and Phase Composition of Nanostructured Ag<sub>2</sub>S Silver Sulfide

## Stanislav I. Sadovnikov<sup>a\*</sup>, Emma G. Vovkotrub<sup>b</sup>

<sup>a</sup> Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, Ekaterinburg 620990, Russia <sup>b</sup> Institute of High-Temperature Electrochemistry, Ural Branch of the Russian Academy of Sciences, Ekaterinburg 620137, Russia

#### ABSTRACT

The thermal stability of phase composition and particle size of nanocrystalline silver sulfide Ag<sub>2</sub>S powder has been examined for the first time by *in situ* high-temperature X-ray diffraction, scanning electron microscopy and Raman spectroscopy methods. It was shown that in oxidizing environment or in the presence of oxidizing impurities, heating of nanostructured silver sulfide is accompanied by its decomposition (dissociation) with isolation of metallic silver. Reduction of silver sulfide particles leads to decreasing the decomposition temperature of Ag<sub>2</sub>S. The decomposition of Ag<sub>2</sub>S nanopowder with isolation of silver metal as a result of heating in air by high-power laser radiation was confirmed by Raman scattering. In the absence of oxidizing environment, heating of silver sulfide does not lead to its decomposition and nanoparticle growth up to the temperature of ~450 K. The nanoparticle size increases as a result of annealing at a temperature of 450-930 K corresponding to the region of collective recrystallization of silver sulfide nanopowder. For nanostructured silver sulfide, the activation energy Q of collective recrystallization in the temperature range 450-900 K is ~0.12 eV·atom<sup>-1</sup>.

Key words: Nanostructured silver sulfide, Thermal stability of nanoparticle size, Decomposition, Silver whiskers

<sup>&</sup>lt;sup>\*</sup> Corresponding author. Institute of Solid State Chemistry, Russian Academy of Sciences, Ekaterinburg, 620990, Russia.

E-mail address: sadovnikov@ihim.uran.ru (S.I. Sadovnikov).

#### **1. Introduction**

Metal sulfide semiconductor nanostructures represent the most promising group of nanostructured materials with excellent optical and electrical properties for various applications [1-3]. Among them, much attention is drawn to nanostructured silver sulfide Ag<sub>2</sub>S [4-6], which is a semiconductor below ~450 K and a superionic conductor at T > 452 K.

Silver sulfide Ag<sub>2</sub>S has three polymorphic modifications [6]. The low-temperature monoclinic (space group 14 -  $P2_1/c$ ) semiconducting phase  $\alpha$ -Ag<sub>2</sub>S (acanthite) exists at temperatures to ~452 K. Argentite  $\beta$ -Ag<sub>2</sub>S has a body-centered cubic (space group 229 -  $Im\bar{3}m$ ) crystal lattice and exists in the temperature interval 452-859 K. The high-temperature face-centered cubic (space group  $N_2$  225 -  $Fm\bar{3}m$ ) phase  $\gamma$ -Ag<sub>2</sub>S is stable at temperatures from ~860 K to melting temperature.

Silver sulfide, as one of the most versatile semiconductors, can be used in photoelectrochemical cells, photocells, photoconductors and infrared detectors [6-9].

Silicon and germanium containing semiconductors are the basis of modern electronic engineering. The maximum operating temperature of germanium devices does not exceed 323-330 K, for silicon devices it increases to 400-430 K. Silicon exhibits a better operation stability at high temperatures. However, with further application of Si and other accepted semiconductors, the improvement of the performance and stability of integrated circuits by increasing the operating clock frequency and the number of transistors is becoming an ever more complicated and expensive task. The point is that the heat release of transistors increases exponentially as their switching speed increases. Therefore, an important challenge is to determine the regions of thermal stability of semiconducting compounds and materials that are potentially suitable for operation at elevated temperatures. One of such materials is nanostructured silver sulfide.

Potential application of nanostructured silver sulfide holds much promise in micro- and nanoelectronics, where Ag<sub>2</sub>S/Ag heteronanostructures are used in nonvolatile memory devices and resistive switches. Their action is based on reduction of Ag<sup>+</sup> cations of silver sulfide to metallic Ag atoms, transformation of acanthite  $\alpha$ -Ag<sub>2</sub>S into argentite  $\beta$ -Ag<sub>2</sub>S and appearance of a conducting channel from Ag and argentite  $\beta$ -Ag<sub>2</sub>S [10-15]. Hybrid heteronanostructures Ag<sub>2</sub>S/Ag exhibit enhanced efficiency in photocatalysis owing to their band structure peculiarities [16-18].

As a rule, microelectronic devices and photocatalysts, having a nanostructured silver sulfide cell, operate in air at elevated temperatures (to ~400-450 K), at which the growth and variation in the phase composition of  $Ag_2S$  nanoparticles may take place, leading to the degradation of

their electrical and optical properties. For example, according to data [19], the fluorescence maximum of photoluminescence emission spectra changes from 975 to 1175 nm when the size of  $Ag_2S$ quantum dots in colloidal solutions increases from 2.4 to 7.0 nm; according to [5, 6], the same shift of the fluorescence maximum from ~960 to ~1176 nm occurs when the size of  $Ag_2S$  quantum dots increases from 2.3 to 15.0 nm. The observed shift is due to the weakening of the quantum confinement effect (quantum localization) and decreasing the band gap  $E_g$  as a result of  $Ag_2S$ quantum dot growth. This agrees with the experimental data [20] on the dimensional dependence of the band gap of  $Ag_2S$  nanopowders.

The uncontrolled growth of quantum dot and  $Ag_2S$  nanoparticle dimensions results in the instability and degradation of properties of devices and compositions with nanostructured silver sulfide.

When studying the thermal stability of nanostructured silver sulfide, special attention should be paid to the phase transformation of the semiconductor monoclinic acanthite  $\alpha$ -Ag<sub>2</sub>S to the superionic cubic argentite  $\beta$ -Ag<sub>2</sub>S at a temperature of ~448-450 K. The cubic argentite  $\beta$ -Ag<sub>2</sub>S has a very high mobility of Ag<sup>+</sup> ions. This is due to its crystal structure, in which four silver atoms are statistically distributed in 54 positions 6(*b*) and 48(*j*) with probabilities 0.0978 and 0.0711, respectively [6, 21].

The least distance between the Ag1 and Ag1 atoms in the crystal lattice of monoclinic  $\alpha$ -Ag<sub>2</sub>S acanthite at 433 K is equal to 0.3353 nm, and the least distance between the Ag1 and Ag2 atoms is in the interval from 0.3087 to 0.3205 nm [22, 23]. In cubic  $\beta$ -Ag<sub>2</sub>S argentite, possible distances between silver atoms at a similar temperature of 453 K are much smaller. According to [22, 23], in the crystal lattice of cubic  $\beta$ -Ag<sub>2</sub>S argentite at 453 K the least possible distances between the Ag1 and Ag1 atoms are equal to 0.2431 nm, between the Ag1 and Ag2 atoms the least distances lie in the range from 0.0927 to 0.3256 nm, and between the Ag2 and Ag2 atoms the least distances are from 0.0561 to 0.3002 nm. The covalent radius of Ag atom is ~0.146 nm, and ionic radius of Ag<sup>+</sup> is ~0.126 nm. With that in mind, it is clear that silver atoms in monoclinic acanthite are at rather large distances from each other and therefore they occupy their crystallographic sites with probability 1. In cubic  $\beta$ -Ag<sub>2</sub>S argentite, the possible distances between silver atoms are too small for 6(b) and 48(j) positions to be occupied by Ag atoms with probability 1. For this reason, the occupancies of the 6(b) and 48(j) positions by Ag atoms (put it otherwise, the probabilities of finding Ag atoms in the 6(b) and 48(i) sites) are very small, less than 0.1 [6, 21, 23]. Physically, this means that 4 silver atoms in the superionic argentite lattice are in continuous motion over 54 possible crystallographic positions. With time, the continuous motion of Ag atoms (ions) can lead

to Ag<sub>2</sub>S nanoparticles growth and to a decrease in the thermal stability of devices based on nanostructured silver sulfide operating at elevated temperature.

There is scarcely any information in the literature on the variation in the size and phase composition of particles (grains) of nanostructured sulfides with temperature and on their recrys-tallization. We can mention only the work [24] on recrystallization of cadmium sulfide films, in which the grain size variation was not discussed, and the study [25] devoted to recrystallization in lead sulfide nanofilms.

As for nanostructured silver sulfide, the information about its thermal properties is limited to works [22, 23, 26-28] dealing with the effect of Ag<sub>2</sub>S particle size on the thermal expansion coefficient and heat capacity. Even the recent review article [5] devoted to nanostructured silver sulfide and monograph [6] contain no information about the effect of temperature on the phase composition and size of silver sulfide nanoparticles. Limited data on the effect of temperature on the size of Ag<sub>2</sub>S nanoparticles and the recrystallization of silver sulfide nanopowders are presented in work [29]. Besides, the phase transformation of acanthite  $\alpha$ -Ag<sub>2</sub>S into argentite  $\beta$ -Ag<sub>2</sub>S takes place in silver sulfide at ~448-450 K. It is not known how this phase transformation affects the recrystallization and the silver sulfide nanoparticle growth.

In this connection, in the present work the effect of temperature and phase transformation "acanthite - argentite" on the particle size and phase composition of nanostructured silver sulfide was studied experimentally for the first time, and the regions of thermal stability and recrystallization of  $Ag_2S$  nanoparticles were determined.

#### 2. Experimental details

Silver sulfide powders were synthesized by chemical deposition from aqueous solutions of silver nitrate AgNO<sub>3</sub>, sodium sulfide Na<sub>2</sub>S and sodium citrate Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>. The solubility product  $K_{sp}$  of silver sulfide Ag<sub>2</sub>S is very small (at 298 K  $K_{sp} = 6.3 \cdot 10^{-50}$  [6, 30]) and deposition of silver sulfide occurs by the following reaction scheme

$$2\operatorname{AgNO}_3 + \operatorname{Na}_2 S \xrightarrow{\operatorname{Na}_3 C_6 H_5 O_7} \operatorname{Ag}_2 S \downarrow + 2\operatorname{NaNO}_3.$$
(1)

Ag<sub>2</sub>S powders with different particle size were prepared from the same chemical reagents by changing their concentration in the solution.

In this work, silver sulfide powders with the average particle size of less than 50 nm are considered as nanocrystalline, while those with the average particle size of about 200 nm are called bulk powders. The procedure of synthesis of coarse- and nanocrystalline Ag<sub>2</sub>S powders is described elsewhere [31, 32] (*see also* Supplementary material for experimental details).

The high-temperature *in situ* X-ray diffraction (XRD) studies were carried out on a STA-DI-P (STOE) diffractometer in Debye-Scherrer geometry. The diffractometer was equipped with a quartz capillary furnace STOE. For better determination accuracy of lattice parameters, measurements were performed in Cu*K* $\alpha_1$ -radiation in angle interval  $2\theta = 20-55^{\circ}$  with a step of  $\Delta(2\theta) = 0.02^{\circ}$  and scanning time of 50 s in point. The quartz capillary was filled by a silver sulfide powder, the diameter of quartz capillary was 0.3 mm. The diffraction measurements were carried out with the use of a linear position-sensitive detector while continuous rotation of the capillary at a temperature from 295 to 773 K with a step of ~25-30 K.

In addition, the high-temperature *in situ* X-ray measurements of Ag<sub>2</sub>S nanopowders were conducted on an X`Pert PRO MPD (Panalytical) diffractometer in Bragg-Brentano geometry. The diffractometer was furnished with a fast position-sensitive solid-state sector detector PIXCEL and an Anton Paar HTK-1200 Oven providing heating of samples. The diffraction measurements were carried out at a temperature from 295 to 398 K in Cu $K\alpha_{1,2}$ -radiation in the angle interval  $2\theta = 20$ - $67.5^{\circ}$  with a step of  $\Delta(2\theta) = 0.026^{\circ}$  and scanning time of 200 s in point.

The synthesized silver sulfide powders were also examined on a Shimadzu XRD-7000 diffractometer in  $CuK\alpha_1$ -radiation in the angle interval  $2\theta = 20.95^\circ$  with a step of  $\Delta(2\theta) = 0.02$  and scanning time of 10 s in point. The determination of the crystal lattice parameters and final structure refinement of the synthesized silver sulfide powders were performed by means of the X'Pert HighScore Plus software suite [33].

The nanocrystalline silver sulfide powders were additionally annealed in vacuum 0.013 Pa at 393, 423, 453 and 493 K for 2 h and heated to the annealing temperature  $T_{ann}$  at a rate of not more than 1 K·min<sup>-1</sup>, as well as in argon atmosphere during heating to 623 K for 2 h at a rate of 1 K·min<sup>-1</sup>.

The average size D of particles (to be more precise, the average size of coherent scattering regions (CSR)), in the synthesized silver sulfide nanopowders was estimated by the XRD method from  $\beta(2\theta)$  diffraction reflection broadening using the dependence of the reduced reflection broadening  $\beta^*(2\theta) = [\beta(2\theta)\cos\theta]/\lambda$  on the scattering vector  $s = (2\sin\theta)/\lambda$  [34, 35] (see Supplementary material). The diffraction reflections were described by the pseudo-Voigt function. The particle size was found also from the value of specific surface  $S_{sp}$ , measured by the Brunauer-Emmett-Teller (BET) method, and from scanning electron microscopy data.

The changes occurring during heating of silver sulfide powders were observed directly using the scanning electron microscopy (SEM) method on a JEOL-JSM LA 6390 microscope with a

JED 2300 Energy Dispersive X-ray Analyzer. The elemental composition of  $Ag_2S$  powders was obtained on the same microscope by means of EDX analysis.

Nanostructured silver sulfide was examined by transmission electron microscopy (TEM) method. The high-resolution TEM images were recorded on a JEOL JEM-2010 transmission electron microscope with 0.14 nm (1.4 Å) lattice resolution.

The Raman spectra were measured on a RENISHAW-1000 (Renishaw plc., UK) microscope-spectrometer with visible continuous radiation in the "green" spectral region at wavelength 532 nm, and at radiation power to 40 mW in the interval 50-4000 cm<sup>-1</sup>. The measurement conditions were as follows: spectrograph diffraction grating with 1800 groove·mm<sup>-1</sup>; exciting radiation power on sample was from 0.4 to 40 mW; accumulation (exposure) time of one spectrum was from 10 to 30 s; and number of scans (number of signal accumulation cycles) was equal from 2 to 10 (*see* Supplementary material).

#### 3. Results and discussion

The thermal stability of nanostructured silver sulfide was studied on powders with an average CSR size of about 45 and 85 nm (from XRD data). According to BET data, the particle size in these powers is ~45 and ~163 nm. Comparison of particle sizes determined by XRD and BET methods shows that the coarser powder was agglomerated. The TEM image of  $Ag_2S$  nanoparticle with a size about 40 nm of synthesized silver sulfide nanopowder is demonstrated in Fig. 1.

#### 3.1. Decomposition of silver sulfide in oxidizing medium

The XRD patterns were recorded in Debye-Scherrer geometry in air at a temperature from 295 to 773 K for Ag<sub>2</sub>S powder with CSR size equal to 85 nm. Film strip *in situ* XRD plots are shown in Fig. 2, and their evolution in standard coordinates " $2\theta$  angle - intensity" is presented in Fig. 3.

Full-profile structure refinement and comparison with data [31, 32] revealed that diffraction reflections of monoclinic (space group  $P2_1/c$ ) acanthite  $\alpha$ -Ag<sub>2</sub>S are observed on the XRD plots during heating up to 448 K (Fig. 2, 3). At further heating from 453 to 623 K, the XRD plots contain diffraction reflections of cubic (space group  $Im\bar{3}m$ ) argentite  $\beta$ -Ag<sub>2</sub>S. Thus, the transformation of acanthite into argentite takes place at ~450 K. At 673 K, along with argentite reflections, diffraction reflections of cubic (space group  $Fm\bar{3}m$ ) Ag metal appear on the XRD pattern, while at higher temperatures, 723 and 773 K, the XRD patterns contain only diffraction reflections of silver. This is due to the following reasons.

The peculiarity of silver sulfide in comparison with other sulfides is its stability to oxidation because coarse-crystalline (bulk) Ag<sub>2</sub>S does not interact with oxygen during heating in air to ~770 K. Only as a result of calcinations in air at a temperature of >800 K, coarse-crystalline silver sulfide with particle size of more than 2-3  $\mu$ m is decomposed with isolation of silver metal and sulfur, which is oxidized to gaseous sulfur dioxide (sulfurous gas):

$$Ag_2S + O_2 \rightarrow 2Ag + SO_2 \uparrow.$$
<sup>(2)</sup>

A similar spontaneous isolation of silver in the form of whiskers during heating of  $Ag_2S$  to 800-900 K was noted in study [36]. The formation of silver whiskers on the surface of pressed  $\alpha$ -Ag<sub>2</sub>S pellet heated in air up to 570 K was observed in work [37].

In oxidizing medium, reduction of silver sulfide particles leads to lowering of its decomposition temperature and to the appearance of metallic silver at lower temperature.

Indeed, heating of the synthesized silver sulfide nanopowder at a rate of  $5 \text{ K} \cdot \text{min}^{-1}$  and more in vacuum 0.013 Pa ( $10^{-4} \text{ mm Hg}$ ) or in argon or helium atmosphere under pressure  $1.01 \times 10^{5}$ Pa to  $\geq 623$  K is accompanied by the formation of silver metal. Figure 4 shows as an example the variation in the XRD plot of Ag<sub>2</sub>S nanopowder with particle size ~45 nm after heating in argon atmosphere to 623 K at a rate of 10 K·min<sup>-1</sup>. According to the XRD data, both Ag<sub>2</sub>S powders contain monoclinic (space group  $P2_1/c$ ) acanthite  $\alpha$ -Ag<sub>2</sub>S as basic phase (Fig. 4). The average size *D* of the coherent scattering regions of nanopowders was estimated from the broadening of nonoverlapping diffraction reflections (1 1 0), (-1 1 3), (-1 0 4) and (0 3 1). As a result of heating, the size of powder particles increased from ~45 to ~147 nm, and about 3.5 wt.% silver metal appeared in the powder.

The reason of isolation of metallic silver during rapid heating of the synthesized silver sulfide nanopowder in vacuum or argon is oxidation of some part of sulfur in the sulfide by oxygen or moisture adsorbed by the nanopowder surface, removal of sulfur in the form of gaseous  $SO_2$  and, as a consequence, liberation of some amount of silver.

Scanning electron microscopy of the synthesized  $Ag_2S$  nanopowder (Fig. S1, *see* Supplementary material) and the sample pressed from the same powder and annealed for 2 h in vacuum at 773 K (Fig. 5) confirms the variation in the phase composition as a result of isolation of metallic silver whiskers. Figure S1 (*see* Supplementary material) demonstrates a SEM image of the initial  $Ag_2S$  nanopowder and the size distribution of nanoparticles in this nanopowder. The average nanoparticle size is ~45 nm. After heating to 773 K, numerous silver metal whiskers 1-2 µm in diameter and 1 mm and more in length appeared on the surface of the pressed  $Ag_2S$  nanopowder sample (Fig. 5*a*). Energy dispersive X-ray analysis of the surface of compact sintered sample at point

(001) has shown that the content of silver Ag and sulfur S is ~96.5 $\pm$ 0.4 and ~3.5 $\pm$ 0.1 wt.%, respectively (Fig. 5*b*). The content of silver, which is almost 10 wt.% larger than in silver sulfide Ag<sub>2</sub>S, confirms the decomposition of silver sulfide. In some places, the whiskers form splices (aggregates) to 40 µm in thickness (Fig. 5*c*). The isolation of silver metal on the surface of compact sample sintered at 773 K is observed visually (Fig. 6).

In order to avoid, during temperature variations, the loss of a part of sulfur caused by its oxidation by adsorbed moisture and oxygen impurities, silver sulfide nanopowders were preliminarily annealed in vacuum 0.013 Pa ( $10^{-4}$  mm Hg). Slow heating in vacuum to the annealing temperature 393 K was performed for 2 h at a rate of 0.5 K·min<sup>-1</sup>, then the nanopowders were annealed for 2 h at 393 K in vacuum. Heating of annealed silver sulfide nanopowders did not lead to the isolation of metallic silver. According to differential thermal analysis data, when annealed Ag<sub>2</sub>S nanopowders were heated there is no loss of mass of these nanopowders.

Ag<sub>2</sub>S nanopowder with the average particle size  $\sim$ 45 nm was also studied with the use of Raman spectroscopy. Raman spectroscopy is a qualitative nondestructive analytical method for the identification of different silver compounds, whose vibrational frequencies are in the near IR range. Interfering impurities, such as H<sub>2</sub>O and CO<sub>2</sub>, have no effect on the Raman spectroscopy results.

Raman spectroscopy of  $Ag_2S$  at the maximal exciting radiation power of 40 mW provided high intensity, but led simultaneously to photoinduced decomposition of silver sulfide, which manifested itself in the appearance of a very sharp peak at 1437 cm<sup>-1</sup> and strong peaks at ~490 and ~1250 cm<sup>-1</sup> (Fig. S2*b*, *see* Supplementary material). According to [38, 39], the observed strong peaks at ~490, ~1250 and 1437 cm<sup>-1</sup> correspond to vibrations of metallic silver Ag and sulfur oxide compounds that are isolated during photoinduced decomposition of Ag<sub>2</sub>S in air. Indeed, the observation of Ag<sub>2</sub>S powder by means of optical microscope after irradiation and registration of Raman spectra showed that the sample became black in the irradiation region (Fig. S2*a*, Supplementary material). Even the registration of spectra at a decreased laser radiation power of 4 mW (10 % of the maximal power) and with a small number of scans did not allow us to eliminate Ag<sub>2</sub>S decomposition completely and to get rid of decomposition-related peaks at ~490, ~1250 and 1437 cm<sup>-1</sup>.

At the background of strong peaks due to silver sulfide photodecomposition, the intensity of bands related immediately to Ag<sub>2</sub>S is small.

The survey Raman spectrum of  $Ag_2S$  nanopowder recorded at exciting radiation power of 10 mW (25 % of the maximal power) and by only two scans of the sample is displayed in Fig. 7*a*.

It is similar to the spectrum of fine silver sulfide powder with monoclinic acanthite structure reported in work [38]. The Raman spectrum of  $\alpha$ -Ag<sub>2</sub>S nanopowder in the low-frequency range 210-260 cm<sup>-1</sup> is smeared and broadened. For more detailed analysis, Figs. 7*b* and 7*c* show the spectra of  $\alpha$ -Ag<sub>2</sub>S nanopowder in the low-frequency region recorded by us in work [40] at 10-fold scanning of the sample and radiation power of 10 and 4 mW, respectively.

The spectra (Figs. 7b, 7c) contain a series of bands in the interval 90-260 cm<sup>-1</sup>. Besides the bands at 93 and 147 cm<sup>-1</sup>, related to silver sublattice vibrations [38], other bands are observed, which are due to Ag-S bonds and symmetric Ag-S-Ag longitudinal modes. This agrees with the literature data [39, 41, 42], according to which the Raman spectrum of acanthite  $\alpha$ -Ag<sub>2</sub>S is characterized by intense bands at ~93, ~122, 167-188, 225-253 and ~430 cm<sup>-1</sup>. According to [41-43], the peak at ~430 cm<sup>-1</sup> corresponds directly to low-temperature monoclinic acanthite  $\alpha$ -Ag<sub>2</sub>S. The presence of a broad band in the region 210-260 cm<sup>-1</sup> centered at ~240 cm<sup>-1</sup> agrees also with the data of work [44], in which the peak induced by  $Ag_2S$  nanoparticles is observed at ~220 cm<sup>-1</sup>. In the structure of  $\alpha$ -Ag<sub>2</sub>S acanthite, the triatomic Ag-S-Ag chains are non-linear therefore the Raman spectrum bands are related to the symmetric Ag-S-Ag longitudinal vibrational modes. In study [44], Ag<sub>2</sub>S nanoparticles were modeled by a set of  $(AgS)_n$  clusters with n = 1-9 having the minimal energy. Model clusters  $(AgS)_n$  were formed by different number *n* of Ag-S pair bonds. The simulation with the use of the Density Functional Theory approximation revealed that the bands observed in the Raman spectrum of Ag<sub>2</sub>S nanoparticles in the region of ~250 cm<sup>-1</sup> are mainly due to the radial breathing modes of (AgS)<sub>7</sub> cluster, as well as (AgS)<sub>6</sub> and (AgS)<sub>8</sub> clusters (Fig. 8) [44]. According to [43, 45], the fundamental modes that are observed at ~220 and ~430 cm<sup>-1</sup> correspond to the first and second order longitudinal optical phonon modes in Ag<sub>2</sub>S, respectively.

On the whole, Raman scattering confirmed that synthesized silver sulfide nanopowder has a monoclinic structure of the  $\alpha$ -Ag<sub>2</sub>S acanthite type.

#### 3.2. The thermal stability of Ag<sub>2</sub>S nanoparticle size

The effect of temperature on the nanoparticle size was examined on preliminarily annealed silver sulfide nanopowders that did not contain any adsorbed moisture or oxygen impurities.

The *in situ* XRD patterns of annealed nanocrystalline silver sulfide, recorded at 295, 323, 348, 373 and 398 K in air (Fig. 9), contain an identical set of broadened diffraction reflections corresponding to nonstoichiometric monoclinic (space group  $P2_1/c$ ) acanthite  $\alpha$ -Ag<sub>1.93-1.98</sub>S [4]. The average size *D* of coherent scattering regions in initial powder is equal to 43±6 nm, and it agrees

with the size of nanoparticles according to the SEM data. Gradual heating of nanopowder to 398 K did not lead, within the measurement error, to any noticeable narrowing of diffraction reflections, i. e. it was not accompanied by an increase in the nanoparticle size, although the resolution of diffraction reflections in the region of  $2\theta < 28^{\circ}$  weakened. The average CSR size in acanthite nanopowder was estimated is to be  $46\pm6$  nm at 398 K.

The silver sulfide nanopowder was additionally annealed in vacuum 0.013 Pa at the annealing temperature  $T_{ann}$  equal to 393, 423, 453 and 493 K. Besides, a sample was pressed from silver sulfide nanopowder, which was annealed in vacuum at 930 K. Heating to the annealing temperature  $T_{ann}$  was carried out for 2 h. The XRD plots of silver sulfide nanopowder, measured after vacuum annealing at 393, 423, 453, 493 and 930 K (Fig. S3, *see* Supplementary material), contain the diffraction reflections corresponding to nonstoichiometric monoclinic (space group  $P2_1/c$ ) acanthite  $\alpha$ -Ag<sub>1.95-1.98</sub>S.

With allowance for errors of *D* size estimation, two-hour annealing at a temperature to 423 K did not lead to any size gain. A weak growth of the CSR size was observed only for the nanopowders annealed at 453 and 493 K (Fig. S3, Supplementary material). An appreciable increase in the CSR size to 260 nm was observed for the sample annealed at 930 K (Fig. S3, Supplementary material). The value of microstrains, which is ~0.1 % in the initial nanopowder, decreased to ~0.03-0.05 % as a result of annealing.

In the nanopowder annealed in argon atmosphere at 623 K for 2 h, the CSR size of monoclinic acanthite  $\alpha$ -Ag<sub>2</sub>S was 147±10 nm (*see* Fig. 4).

The variation in the Ag<sub>2</sub>S nanoparticle size vs the temperature of vacuum annealing is shown in Fig. 10. At  $T_{ann} < 440$  K, the nanoparticle size hardly changes with increasing  $T_{ann}$  with consideration for the measurement errors, therefore the temperature interval 273-443 K can be treated as the region of thermal stability of Ag<sub>2</sub>S nanoparticle size. The observed nanoparticle growth takes place at  $T_{ann} > 455$  K, although even in the temperature range 460-930 K silver sulfide particles remain nanosized and do not reach the micrometer dimensions. The temperature range 460-930 K, in which the particle size begins to grow appreciably and increases 3-6 times, corresponds to the region of collective recrystallization of silver sulfide nanopowder. Note that the transition from the region of thermal stability of Ag<sub>2</sub>S nanoparticle size to the region of collective recrystallization occurs at a temperature close to the temperature of the phase transformation "acanthite  $\alpha$ -Ag<sub>2</sub>S – argentite  $\beta$ -Ag<sub>2</sub>S" equal to ~450 K [23, 26]. The scanning electron microscopy of Ag<sub>2</sub>S samples annealed at 623 and 930 K (Fig. 10, insets on the right) confirmed the Ag<sub>2</sub>S particles size found from XRD data.

The variation in the average particle (grain) size during collective recrystallization in nanomaterials is related to its duration t by the general ratio  $(D^n - D_0^n) \sim t$ , where n = 1-4 [29, 46]. Grain growth (collective recrystallization) takes place as a result of chemical diffusion, when the concentration gradient is absent, but there is a non-zero gradient of chemical potential. The difference in the chemical potential between particles of different size is due to the contribution from the surface energy to the total energy of particle. The smaller is the particle size, the larger is the relative value of this contribution, therefore, under otherwise equal conditions, small particles possess excess energy as compared with large particles. Hence it is clear that the thermodynamic reason of spontaneous particle growth in polycrystalline substance is reduction of the total energy of the system in this process. If the particle growth is due only to a decrease in the total surface energy of the system as a result of diffusion, then the variation in the particle size D in the process of recrystallization is described by the expression

$$D^2 - D_0^2 = kt , (3)$$

where  $D_0$  is the initial particle (grain) size, *t* is the duration of annealing, and *k* is a coefficient exponentially depending on temperature.

However, recrystallization is a more complex process than diffusion and it does not reduce to the latter. Collective recrystallization is characterized by the activation energy Q. There is no available information in the literature about the activation energy of collective recrystallization in sulfides, especially nanocrystalline ones. In works [47, 48] it was shown by the example of uranium dioxide, aluminum nitride, titanium boride and other nanostructured substances and materials that the variation in the grain size D in the process of collective recrystallization is described by the expression

$$D^{3} - D_{0}^{3} = k_{0} t \exp(-Q/RT), \qquad (4)$$

where  $k_0$  is a normalizing factor. At equal annealing duration t, expression (4) can be written as

$$D^{3} - D_{0}^{3} = k_{t=const} \exp(-Q/RT) .$$
(5)

From Eq. (5) it follows that the larger is the activation energy, the smaller is the particle size, other factors being equal.

The dependence between the silver sulfide nanoparticle size D and the annealing temperature, presented in Fig. 10, can be described in the first approximation by function (5). In accordance with the experimental data, the value of  $D_0$  was assumed to be 45 nm. Quantitative minimization of the D(T) dependence by function (5) with account of  $D_0$ = 45 nm [29] revealed that the acti-

vation energy Q of collective recrystallization for nanostructured silver sulfide in the temperature range 450-900 K is equal to ~33.6 kJ·mol<sup>-1</sup> (~0.35 eV per Ag<sub>2</sub>S formula unit or ~0.12 eV·atom<sup>-1</sup>). Note that the thermal stability of Ag<sub>2</sub>S nanoparticle size is smaller than that for PbS lead sulfide nanoparticles [25]. The growth of Ag<sub>2</sub>S nanoparticles begins at ~460 K, whereas PbS nanoparticles begin to grow at ~700 K. Apparently, the smaller region of the thermal stability of Ag<sub>2</sub>S nanoparticle size is due to a smaller melting temperature of silver sulfide ( $T_{melt}$  for bulk Ag<sub>2</sub>S and PbS is 1115 and 1391 K, respectively). Another reason for the smaller thermal stability of Ag<sub>2</sub>S nanoparticles can be the presence of a phase transformation in silver sulfide at ~450 K; there are no polymorphic phase transitions in lead sulfide. It can be assumed that the transition of Ag<sub>2</sub>S to the region of collective recrystallization is associated with a sharp spasmodic jump in the mobility of silver atoms in the transformation of semiconductor acanthite to superionic argentite.

#### 4. Conclusion

Heating of nanocrystalline silver sulfide powder in air or in oxidizing media (moisture and oxygen adsorbed by the nanopowder surface) leads to its decomposition with isolation of silver metal. The reduction of silver sulfide particles results in a decrease of the decomposition temperature and in the appearance of metallic silver at lower temperature.

The Raman studies confirmed the decomposition of  $Ag_2S$  nanopowder with isolation of metallic silver as a result of heating by high-power laser radiation.

The monoclinic  $\alpha$ -Ag<sub>2</sub>S acanthite-type structure of the synthesized silver sulfide nanopowder was confirmed by Raman scattering. The observation of multiple resonant Raman peaks indicated that the yielded Ag<sub>2</sub>S nanoparticles have good optical properties and crystallinity.

The absence of oxidizing impurities (adsorbed moisture and oxygen) in silver sulfide nanopowder provides a stable phase composition and the absence of decomposition during heating in vacuum or in protective atmosphere of inert gas.

The elevation of the annealing temperature of nanocrystalline  $Ag_2S$  powder from 300 K up to ~450 K leads to an insignificant growth of nanoparticles and to annealing of microstrains, which allows one to consider this temperature range to be a region of thermal size stability of nanocrystalline silver sulfide powder. It means that the electronic devices based on nanostructured silver sulfide may steadily operate in this temperature interval. The temperature interval from 450 to 900 K, where the particle size increases 3-6 times, corresponds to the region of collective recrystallization of silver sulfide nanopowder.

#### Acknowledgements

This study was supported by the Russian Science Foundation (grant no. 14-23-00025) through the Institute of Solid State Chemistry of the Ural Branch of the RAS. Authors are grateful to Dr. A.P. Tyutyunnik for the help in high-temperature XRD study and to Prof. A.I. Gusev for useful discussion.

# Appendix A. Supplementary data

Supplementary data related to this article can be found at ...

#### References

- L. Argueta-Figueroa, O. Martínez-Alvarez, J. Santos-Cruz, R. Garcia-Contreras, L.S. Acosta-Torres, J. de la Fuente-Hernández, M.C. Arenas-Arrocena, Mater. Sci. Eng. C. Mater Biolog. Appl. 76 (2017) 1305-1315.
- [2] P. Kulkarni, S.K. Nataraj, R.G. Balakrishna, D.H. Nagaraju, M.V. Reddy, J. Mater. Chem. A 5 (2017) 22040-22094.
- [3] Y. Xiao, S.H. Lee, Y.-K. Sun, Advanc. Energy Mater. 7 (2016) paper 1601329 (20 pp).
- [4] A. Tang, Yu. Wang, H. Ye H, C. Zhou, C. Yang, X. Li, H. Peng, F. Zhang, Y. Hou, F. Teng, Nanotechnology 24 (2013) paper 355602 (12 pp).
- [5] S.I. Sadovnikov, A.I. Gusev, J. Mater. Chem. A 5 (2017) 17676-17704.
- [6] S.I. Sadovnikov, A.A. Rempel, A.I. Gusev, Nanostructured Lead, Cadmium and Silver Sulfides: Structure, Nonstoichiometry and Properties, Springer Intern. Publ. AG, Cham - Heidelberg, 2018. 317 pp.
- [7] W. Zhang, L. Zhang, Z. Hui, X. Zhang, Y. Qian, Sol. State Ionics 130 (2000) 111-114.
- [8] N. Du, H. Zhang, H.Z. Sun, D.R. Yang, Mater. Lett. 61 (2007) 235-238.
- [9] L.H. Dong, Y. Chu, Y. Liu, J. Colloid. Interf. Sci. 317 (2008) 485-492.
- [10] K. Terabe, T. Hasegawa, T. Nakayama, M. Aono, Nature 433 (2005) 47-50.
- [11] C.H. Liang, K. Terabe, T. Hasegawa, V. Aono, Nanotechnology 18 (2007) paper 485202 (5pp).
- [12] Z. Xu, Y. Bando, W. Wang, X. Bai, D. Golberg, ACS Nano 4 (2010) 2515-2522.
- [13] D. Wang, L. Liu, Y. Kim, Z. Huang, D. Pantel, D. Hesse, M. Alexe, Appl. Phys. Lett. 98 (2011) paper 243109 (3 pp).
- [14] S.I. Sadovnikov, A.I. Gusev, J. Nanopart. Res. 18 (2016) paper 277 (12 pp).
- [15] A.I. Gusev, S.I. Sadovnikov, Mater. Lett. 188 (2017) 351-354.
- [16] S.I. Sadovnikov, E.A. Kozlova, E.Yu. Gerasimov, A.A. Rempel, Catal. Commun. 100 (2017) 178-182.
- [17] M. Basu, R. Nazir, C. Mahala, P. Fageria, S. Chaudhary, S. Gangopadhyay, S. Pande, Langmuir 33 (2017) 3178-3186.
- [18] S.I. Sadovnikov, E.A. Kozlova, E.Yu. Gerasimov, A.A. Rempel, A.I. Gusev, Intern. J. Hydrogen Energy 42 (2017) 25258-25266.
- [19] Y. Zhang, Y. Liu, C. Li, X. Chen, Q. Wang, J. Phys. Chem. C 118 (2014) 4918-4923.
- [20] S.I. Sadovnikov, Yu.V. Kuznetsova, A.A. Rempel, Nanostr. Nano-Object. 7 (2016) 81-91.
- [21] S.I. Sadovnikov, A.I. Gusev, A.A. Rempel, Phys. Chem. Chem. Phys. 17 (2015) 20495-20501.

- [22] A.I. Gusev, S.I. Sadovnikov, A.V. Chukin, A.A. Rempel, Phys. Solid State 58 (2016) 251-257.
- [23] S.I. Sadovnikov, A.I. Gusev, A.V. Chukin, A.A. Rempel, Phys. Chem. Chem. Phys. 18 (2016) 4617-4626.
- [24] W. Kahle, H. Berger, Phys. stat. sol.(a) 2 (1970) 717-721.
- [25] S.I. Sadovnikov, N.S. Kozhevnikova, A.A. Rempel, Inorg. Mater. 47 (2011) 837-843.
- [26] S.I. Sadovnikov, A.I. Gusev, Phys. Solid State 59 (2017) 1887-1894.
- [27] S.I. Sadovnikov, A.I. Gusev, J. Thermal Anal. Calorimetry 131 (2018) 1155-1164.
- [28] A.I. Gusev, S.I. Sadovnikov, Thermochim. Acta 660 (2018) 1-10.
- [29] S.I. Sadovnikov, A.I. Gusev, Phys. Solid State 60 (2018) 1308-1315,
- [30] P. Patnaik, Dean's Analytical Chemistry Handbook, 2<sup>nd</sup> ed., McGraw-Hill, New York, 2004. Table 4.2. 1280 pp.
- [31] S.I. Sadovnikov, A.I. Gusev, A.A. Rempel, Superlattices Microstruct. 83 (2015) 35-47.
- [32] S.I. Sadovnikov, A.I. Gusev, A.A. Rempel, Phys. Chem. Chem. Phys. 17 (2015) 12466-12471.
- [33] X'Pert HighScore Plus. Version 2.2e (2.2.5). © 2009 PANalytical B. V. Almedo, the Netherlands.
- [34] A.I. Gusev, A.A. Rempel, Nanocrystalline Materials, Cambridge Intern. Science Publ., Cambridge, 2004. 351 pp.
- [35] S. I. Sadovnikov, A. I. Gusev, J. Alloys Comp. 586 (2014) 105-112.
- [36] T. Blanton, S. Misture, N. Dontula and S. Zdzieszynski, Powder Diffraction 26 (2011) 110-118.
- [37] J. Corish, C.D. O'Briain, J. Mater. Sci. 6 (1971) 252-259.
- [38] I. Martina, R. Wiesinger, D. Jembrih-Simbürger, M. Schreiner, E-Preservation Science: Morana RTD 9 (2012) 1-8.
- [39] J.I. Lee, S.M. Howard, J.J. Kellar, K.N. Han, W. Cross, Metall. Mater. Trans. B 32 (2001) 895-901.
- [40] S.I. Sadovnikov, E.G. Vovkotrub, A.A. Rempel, Doklady Phys. Chem. 480 (2018) 80-82.
- [41] A.N. Belov, O.V. Pyatilova, M.I. Vorobiev, Advanc. Nanoparticles 3 (2014) 1-4.
- [42] G. Socrates, Infrared and Raman characteristic group frequencies: Tables and charts. 3<sup>rd</sup> ed.
   Wiley, Chichester New York, 2001. 347 pp.
- [43] M. Osada, K. Terabe, C. Liang, T. Hasegawa, In: 214<sup>th</sup> ECS Meeting Abstracts MA 2008-2 (214<sup>th</sup> ECS Metting, Honolulu, October 12-17, 2008). Honolulu: ECS, 2008. B10 Solid State Ionic Devices 6 Nano Ionics, 2008. Abstract 1406.

- [44] Y. Delgado-Beleño, M. Cortez-Valadez, C.E. Martinez-Nuñez, R. Britto Hurtado, A.B. Alvarez Ramón, O. Rocha-Rocha, H. Arizpe-Chávez, A. Perez-Rodríguez, M. Flores-Acosta, Chem. Physics 463 (2015) 106-110.
- [45] L. Hashmi, P. Sana, M.M. Malik, A.H. Siddiqui, M.S. Qureshi, Nano Hybrides 1 (2012) 23-43.
- [46] Thesaurus of nanotechnological terms and nanotechnology-related terms / Ed. S.V. Kalyuzhnyi. Fizmatlit, Moscow, 2010. 528 pp. (*in Russian*)
- [47] F.A. Nichols, J. Appl. Phys. 37 (1966) 4599-4602.
- [48] Functional Gradient Materials and Surface Layers Prepared by Fine Particles Technology / Eds. M.-I. Baraton, I.V. Uvarova. Kluwer, Dordrecht, 2001. 317 pp.

16

#### ACCEPTED MANUSCRIPT Figure captions for the paper

"Thermal stability of nanoparticle size and phase composition of nanostructured Ag<sub>2</sub>S silver sulfide" by S.I. Sadovnikov and E.G. Vovkotrub

**Fig. 1**. The TEM image of Ag<sub>2</sub>S nanoparticle with a size about 40 nm of synthesized nanostructured silver sulfide powder.

Fig. 2. The film strip plot of *in situ* high-temperature XRD data for Ag<sub>2</sub>S powder with particle size about 85 nm recorded in Debye-Scherrer geometry on air at a temperature from 298 to 773 K.Fig. 3. Evolution of XRD patterns of silver sulfide powder with the average particle size of ~85 nm

during heating from 298 to 773 K in air. The yellow lines indicate the position of the main reflections of monoclinic acanthite (at 298-453 K) and cubic argentite (at 463-623 K). The intensity is shown in logarithmic scale.

**Fig. 4**. XRD patterns of synthesized silver sulfide nanopowder with the average nanoparticle size of ~45 nm and the same powder after heating from room temperature to 623 K in argon with the heating rate 10 K $\cdot$ min<sup>-1</sup>.

**Fig. 5**. The SEM image of the surface of sample pressed from  $Ag_2S$  nanopowder and annealed for 2 h in vacuum at 773 K: (*a*) metallic silver whiskers 1-2 µm in diameter and 1 mm and more in length; (*b*) elemental EDX analysis of the sample surface at point (001) marked in Fig. 5*a*; (*c*) splices (aggregates) of metallic silver whiskers.

**Fig. 6**. Silver metal isolated on the surface of sample pressed from Ag<sub>2</sub>S nanopowder after 2 h annealing in vacuum at 773 K.

**Fig. 7**. Raman spectra of  $Ag_2S$  nanopowder recorded at room temperature under different scanning conditions: (*a*) the survey spectrum recorded at 2-fold scanning of the sample at radiation power 10 mW, (*b*) and (*c*) the spectra in the low-frequency region recorded at 10-fold scanning of the sample with different radiation power, 10 and 4 mW, respectively.

**Fig. 8**. Most probable  $(AgS)_n$  clusters (with n = 7-9) whose radial breathing modes determine predominately the bands observed in the Ag<sub>2</sub>S nanoparticles Raman spectrum near 250 cm<sup>-1</sup>.<sup>42</sup>

**Fig. 9**. In situ XRD patterns of nanocrystalline acanthite  $\alpha$ -Ag<sub>2</sub>S during heating from 300 to 398 K in air. The insets on the right show the average size of the coherent scattering regions estimated from the broadening of non-overlapping diffraction reflections. The XRD patterns are recorded on an X<sup>Pert</sup> PRO MPD (Panalytical) diffractometer in Bragg-Brentano geometry.

**Fig. 10**. (*a*) The effect of the annealing temperature on the size D of nanoparticles of Ag<sub>2</sub>S powder (the vertical dash-and-dot line denotes the boundary between the thermal stability region of silver sulfide nanoparticle size and the region of collective recrystallization). The thermal stability region in the bottom inset is scaled-up. The insets on the right show the SEM images of Ag<sub>2</sub>S samples after vacuum annealing at (*b*) 623 and (*c*) 930 K.



CER HI











the second second









Silver sulfide nanopowders are prepared by chemical deposition from aqueous solutions. • Thermal stability of  $Ag_2S$  particle size is estimated by *in situ* high-temperature XRD method. • Heating of  $Ag_2S$  up to the temperature of 450 K does not lead to nanoparticle growth. • The nanoparticle size increases as a result of recrystallization at a temperature of 450-930 K. • For nano- $Ag_2S$ , the activation energy of collective recrystallization is 0.12 eV-atom<sup>-1</sup>.