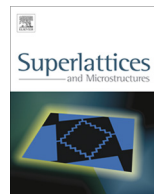




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# Artificial silver sulfide $\text{Ag}_2\text{S}$ : Crystal structure and particle size in deposited powders

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## ABSTRACT

Chemical deposition from aqueous solutions of silver nitrate and sodium sulfide was used for synthesis of coarse-crystalline and nanocrystalline silver sulfide  $\text{Ag}_2\text{S}$  powders. Sodium citrate was used as a complexing and stabilizing agent during synthesis. X-ray diffraction study shows that synthesized  $\text{Ag}_2\text{S}$  powders have monoclinic (space group  $P2_1/c$ )  $\alpha$ - $\text{Ag}_2\text{S}$  acanthite type crystal structure. The unit cell of artificial monoclinic silver sulfide  $\text{Ag}_2\text{S}$  contains four  $\text{Ag}_2\text{S}$  formula units and has the following parameters:  $a = 0.42264$  nm,  $b = 0.69282$  nm,  $c = 0.95317$  nm and  $\beta = 125.554^\circ$ . The size of silver sulfide particles in deposited powders was estimated by the X-ray diffraction and BET methods. By varying the ratio between the concentrations of reagents in the initial reaction mixture it is possible to deposit  $\text{Ag}_2\text{S}$  nanoparticles with average size ranging in the interval from  $\sim 1000$  to  $\sim 30$  nm.  $\text{Ag}_2\text{S}$  nanopowders have no deformation distortions of the crystal lattice practically because the microstrains  $\varepsilon$  in the synthesized powders do not exceed 0.15%. All the  $\text{Ag}_2\text{S}$  powders with different particle size have an identical morphology.

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## 1. Introduction

Semiconducting nanocrystals, quantum dots, nanostructured films of lead, cadmium, zinc and silver chalcogenide have found wide application as functional materials in optoelectronics, sensor

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technology and laser and power engineering [1–7]. For example, thin films of silver sulfide are used in photo conducting and photochemical cells [8,9], in sensors [10], infrared detectors [11] and solar selective coating for conversion of solar energy into electricity [12,13]. Quantum dots of sulfides including  $\text{Ag}_2\text{S}$  begin to be used as fluorescent labels in biology and medicine [14–19].

According to the phase diagram of the system Ag–S [20,21], silver sulfide  $\text{Ag}_2\text{S}$  has three polymorphic modifications: low-temperature monoclinic phase  $\alpha\text{-Ag}_2\text{S}$  (acanthite) existing at temperatures below  $\sim 450$  K;  $\beta\text{-Ag}_2\text{S}$  phase (argentite) with body centered cubic (bcc) sublattice of sulfur atoms existing in the temperature range 452–859 K; and high-temperature face centered cubic (fcc) phase  $\gamma\text{-Ag}_2\text{S}$  stable from  $\sim 860$  K up to melting temperature. In the literature, the designations of monoclinic and bcc phases are often confounded. For example, in works [22–24] monoclinic phase (acanthite) is designated as  $\beta\text{-Ag}_2\text{S}$  and bcc phase (argentite) as  $\alpha\text{-Ag}_2\text{S}$ .

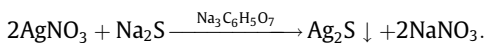
It is thought that monoclinic  $\alpha\text{-Ag}_2\text{S}$  phase is stoichiometric, whereas cubic  $\beta\text{-Ag}_{2\pm\delta}\text{S}$  and  $\gamma\text{-Ag}_{2\pm\delta}\text{S}$  with  $\delta \cong 0.002$  are nonstoichiometric phases having either small deficiency or small excess of silver. The homogeneity regions of cubic allotropic forms of  $\text{Ag}_2\text{S}$  have been determined in works [24–28].

For practical application as a semiconducting photoluminescent material, of most interest is low-temperature monoclinic  $\alpha\text{-Ag}_2\text{S}$  (acanthite) phase in nanosized state. However the crystal structure of this phase was determined mostly on natural samples of acanthite mineral. In this study for the first time the crystal structure of acanthite  $\alpha\text{-Ag}_2\text{S}$  was determined on artificial silver sulfide powder.

## 2. Experimental details

The powders of silver sulfide  $\text{Ag}_2\text{S}$  were synthesized by chemical deposition from aqueous solution of silver nitrate  $\text{AgNO}_3$ , sodium sulfide  $\text{Na}_2\text{S}$  and sodium citrate  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \equiv \text{Na}_3\text{Cit}$ . The concentrations of  $\text{AgNO}_3$ ,  $\text{Na}_2\text{S}$  and  $\text{Na}_3\text{Cit}$  in the reaction mixtures are given in Table 1. Sodium citrate serves as a complexing and stabilizing agent. Besides, in aqueous solutions with a small content of  $\text{S}^{2-}$  ions, sodium citrate can reduce  $\text{Ag}^+$  ions to metallic silver nanoparticles [29,30]. That is why for deposition of silver sulfide without Ag impurity it is necessary to use reaction mixtures with excessive sodium sulfide  $\text{Na}_2\text{S}$ . The concentrations of  $\text{AgNO}_3$ ,  $\text{Na}_2\text{S}$  and  $\text{Na}_3\text{Cit}$  in the reaction mixture C for synthesis of the first coarse-crystalline  $\text{Ag}_2\text{S}$  powder with particle size of  $\sim 500$  nm were 0.05, 0.5 and  $0.005 \text{ mol l}^{-1}$ . The volume of the reaction mixture was 200 ml.

Synthesis was carried out in the following sequence: complexing agent was poured into silver nitrate, then the mixture volume was brought up to 100 ml and the resulting solution was mixed with 100 ml solution of  $\text{Na}_2\text{S}$ . Deposition of silver sulfide occurred by the following reaction scheme



When the reagents are mixed together, silver sulfide is formed almost immediately; as a result, the reaction mixture is discolored to black at first, and then, during one hour,  $\text{Ag}_2\text{S}$  particles deposit and the solution becomes transparent. For the sulfidization reaction to be complete, the deposit was kept in the matrix solution for one day. Deposited  $\text{Ag}_2\text{S}$  was four times washed with distilled water by decanting, filtered and dried in air at 323 K.

**Table 1**

Composition of the initial reaction mixtures, specific surface area  $S_{\text{sp}}$  and average particle size  $D$  of deposited  $\text{Ag}_2\text{S}$  powders.

| No.   | Concentration of reactants in the reaction mixture ( $\text{mol l}^{-1}$ ) |                       |   | $S_{\text{sp}} \pm 0.20$ ( $\text{m}^2 \text{g}^{-1}$ ) | $D$ (nm)     |            |
|-------|--|-----------------------|---|---|--------------|------------|
|       | $\text{AgNO}_3$  | $\text{Na}_2\text{S}$ | $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ |   | BET          | XRD        |
| C     | 0.05   | 0.5                   | 0.005                                       | $1.6 \pm 0.1$   | $515 \pm 15$ | –          |
| $H^a$ | 0.05   | 0.4                   | 0.005                                       | $0.85 \pm 0.1$  | $975 \pm 15$ | –          |
| I     | 0.05   | 0.025                 | 0.025                                       | $19.0 \pm 0.2$  | $44 \pm 5$   | $43 \pm 6$ |
| II    | 0.05   | 0.025                 | 0.0125                                      | $14.9 \pm 0.2$  | $56 \pm 5$   | $46 \pm 8$ |

<sup>a</sup> Hydrothermal chemical deposition.

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