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Effect of small size of particles on thermal expansion and heat capacity of Ag_2S silver sulfide

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ABSTRACT

The thermal expansion and heat capacity of coarse-crystalline (bulk) and nanocrystalline silver sulfide Ag_2S have been studied by dilatometry and differential scanning calorimetry methods in the temperature interval from 290 to 970 K. The thermal expansion coefficient and heat capacity of nanocrystalline silver sulfide in the examined temperature range are larger than the same properties of coarse-crystalline sulfide. It is shown that these differences are due to a small particle size which leads to the restriction of the phonon spectrum on the side of low and high frequencies. It is established that the acanthite α-Ag_2S to argentite β-Ag_2S and argentite β-Ag_2S to γ-Ag_2S phase transformations are the first-order phase transitions, and the temperatures and enthalpies of these transformations have been determined.

1. Introduction

The nanocrystalline silver sulfide Ag_2S attracts recently much attention. This is due to the fact that the particle size reduction to nanosized scale can appreciably change the properties of solid-phase substances, especially semiconductors [1]. The semiconducting nanocrystals and nano-structured films of silver sulfide are used in optoelectronics, infrared equipment and energetic. The application of silver sulfide in Ag_2S/Ag heteronanostructures, which can work as resistive switches and nonvolatile memory devices, holds much promise [2–7]. The operation of resistive switches based on Ag_2S/Ag heteronanostructures is due to the reversible phase transformation of insulating semiconducting acanthite α-Ag_2S into argentite β-Ag_2S having superionic conduction [3,7–12].

For the application of nanocrystalline silver sulfide in infrared equipment, solar energy converters and resistive switches, it is necessary to have information about the variation in the thermal expansion coefficient of different Ag_2S phases versus the temperature and about the effect of particle size on such lattice properties of silver sulfide as heat capacity and thermal expansion.

Silver sulfide Ag_2S has three basic polymorphic modifications [13]. Low-temperature monoclinic phase α-Ag_2S (acanthite) exists at a temperature below ~450 K. Cubic argentite β-Ag_2S has body centered cubic (bcc) sublattice of S atoms and exists in the temperature range 452–859 K. High-temperature cubic phase γ-Ag_2S with face centered cubic (fcc) sublattice of sulfur atoms is stable from ~860 K up to melting temperature. For technical application, of most interest are low-temperature acanthite and argentite phases.

According to Refs. [14,15], the coarse-crystalline silver sulfide with the average particle size of ~500 nm and more has a monoclinic (space group No. 14 – $P2_1/c$ ($P12_1/c1$)) structure of α-Ag_2S acanthite type and is stoichiometric. The unit cell of acanthite α-Ag_2S includes four formula units of Ag_2S ($z = 4$). A thorough study of nanocrystalline silver sulfide revealed that it has the same monoclinic (space group $P2_1/c$) acanthite-type structure, but is nonstoichiometric and has the composition ~$Ag_{1.93}S$ [16].

Argentite β-Ag_2S phase with cubic (space group No 229 – $Im\bar{3}m$ ($I4/m\bar{3}2/m$) (O_h^9)) structure exists at temperatures above 443 K. The unit cell of argentite β-Ag_2S includes two formula units of Ag_2S ($z = 2$). According to high-temperature X-ray diffraction (XRD) data [17], four Ag atoms are statistically distributed in 54 positions 6(b) and 48(j) with the occupation probabilities ~0.097 and ~0.0715, respectively. The structure of argentite β-Ag_2S is described in detail in study [18] and Crystallographic information file (CCDC reference number 1062400) attached thereto, and also in work [19] and Electronic supplementary information (ESI) for this paper [19]. According to Refs. [18,19], four silver atoms are statistically distributed in 6(b) and 48(j) positions with occupation degrees 0.0978(7) and 0.0711(0).

At temperatures above 860 K silver sulfide contains cubic (space group $Fm\bar{3}m$ ($F4/m\bar{3}2/m$) (O_h^5)) γ-Ag_2S phase. The unit cell of γ-Ag_2S phase includes four formula units of Ag_2S ($z = 4$). At a temperature of 923 K eight Ag atoms are statistically distributed in 88 positions 8(c), 32(f) and 48(i) with the occupation probabilities ~0.088, ~0.15, and ~0.027, respectively [17].

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Table 1
Composition of the reaction mixtures for silver sulfide synthesis, content of Ag, S and C in synthesized silver sulfide powders, specific surface area S_{sp} and average particle size D of Ag_2S powders at temperature of 298 K and pressure of $1.01 \cdot 10^5$ Pa.

No.	Concentration of reagents in the reaction mixture ($mol\,l^{-1}$)[a]			Content of Ag, S, and C (wt.%)			S_{sp} [b] ($m^2\,g^{-1}$)	D (nm)	
	$AgNO_3$	Na_2S	$Na_3C_6H_5O_7$	Ag	S	C		BET[c]	XRD[d]
1	0.05	0.1	0.025	86.7 ± 0.4	12.9 ± 0.1	0.4 ± 0.1	1.9 ± 0.1	430 ± 10	–
2	0.05	0.050	0.1	86.8 ± 0.4	12.9 ± 0.1	0.3 ± 0.1	1.8 ± 0.1	460 ± 10	–
3	0.05	0.025	0.1	86.5 ± 0.4	13.0 ± 0.1	0.5 ± 0.1	11.7 ± 0.2	71 ± 5	66 ± 8
4	0.05	0.025	0.025	86.4 ± 0.4	13.1 ± 0.1	0.5 ± 0.1	12.4 ± 0.2	67 ± 5	54 ± 6

[a] Standard uncertainty in determination of concentrations not exceed 0.02 $mol \cdot l^{-1}$.
[b] Standard uncertainty in specific surface area measurements do not exceed 0.1 $m^2 \cdot g^{-1}$ for coarse-crystalline silver sulfide powders, and 0.2 $m^2 \cdot g^{-1}$ for nanocrystalline powders (0.68 level of confidence).
[c] Standard uncertainty in estimation of average particle size from BET measurement do not exceed 10 nm for coarse-crystalline silver sulfide powders, and 5 nm for nanocrystalline powders (0.68 level of confidence).
[d] Standard uncertainty in XRD measurement of average particle size do not exceed 8 nm (0.95 level of confidence).

Under equilibrium conditions, a reversible phase transformation α-Ag_2S − β-Ag_2S takes place at a temperature about 448–453 K, and second reversible phase transformation β-Ag_2S − γ-Ag_2S occurs at a temperature about 845–860 K [13,20–22].

Until recently, few data on the α-Ag_2S − β-Ag_2S and β-Ag_2S − γ-Ag_2S phase transformations were obtained only for coarse-grained (bulk) samples of silver sulfide Ag_2S [20–23]. For example, "α − β" and "β − γ" phase transformations were studied in work [21] and heat capacity measurements of nanocrystalline silver sulfide were carried out in works [18,24]. Lately, dilatometric study of thermal expansion of coarse-crystalline (bulk) and nanocrystalline silver sulfide – monoclinic acanthite α-Ag_2S and cubic argentite β-Ag_2S – has been carried out [19,25].

The information about thermal expansion of silver sulfide is very limited, although such data are necessary for application of Ag_2S at elevated temperatures. According to [26], the linear thermal expansion coefficient α_{ac} of acanthite is equal to $\sim 20 \times 10^{-6}\,K^{-1}$. The temperature interval, to which this coefficient corresponds, and the method of its measurement in work [26] are not given. According to [27], the relative thermal expansions $\Delta L/L$ of coarse-grained (bulk) acanthite in the temperature range 293–450 K and bulk argentite at a temperature from ~460 to 570 K linearly depend on temperature. This implies that the linear thermal expansion coefficients of acanthite and argentite in the mentioned temperature ranges are independent of temperature. Indeed, in the temperature range 293–450 K the linear thermal expansion coefficient α_{ac} of coarse-grained (bulk) acanthite is equal to $16.8 \times 10^{-6}\,K^{-1}$, and the linear thermal expansion coefficient α_{arg} of coarse-grained (bulk) argentite is equal to $45.8 \times 10^{-6}\,K^{-1}$ at a temperature from ~460 to 570 K [27]. According to high-temperature XRD data [19,25], the linear thermal expansion coefficient of coarse-crystalline (bulk) acanthite in the temperature region 300–433 K increases from $\sim 18.4 \times 10^{-6}$ to $\sim 24.0 \times 10^{-6}\,K^{-1}$. The linear thermal expansion coefficient of nanocrystalline acanthite in the same temperature region is almost 25 % more than the same coefficient of coarse-crystalline acanthite. From the measurement of the temperature dependence of the lattice constant of argentite follows that the thermal expansion coefficient of argentite decreases from $\sim 54 \times 10^{-6}$ to $\sim 43 \times 10^{-6}\,K^{-1}$ when the temperature rises from 443 to 623 K [19,25]. However, in the same temperature interval, the lattice constant a of argentite increases from 0.4856 to 0.4894 nm. According to the neutron diffraction data [28], the lattice constant a_{arg} of argentite at 459, 473, 533, and 598 K is 0.4860, 0.4862, 0.4873, and 0.4889 nm, hence $\alpha_{arg} \approx 43 \times 10^{-6}\,K^{-1}$.

The data on the thermal expansion of cubic γ-Ag_2S phase are not available in the literature.

Direct dilatometric measurements of the thermal expansion of coarse-crystalline (bulk) and nanocrystalline silver sulfide at temperatures from 290 to 970 K in the region of existence of monoclinic acanthite α-Ag_2S, cubic argentite β-Ag_2S and cubic γ-Ag_2S phase, as well as the heat capacity measurement of these phases in nanocrystalline state in the temperature interval from 300 to 938 K have been carried out in this work for the first time.

2. Experiments

Coarse-crystalline (bulk) and nanocrystalline silver sulfide powders with different particle size were synthesized by chemical deposition from aqueous solutions of silver nitrate $AgNO_3$, sodium sulfide Na_2S and sodium citrate $Na_3C_6H_5O_7 \equiv Na_3Cit$. The particle size was controlled by varying the reagent concentrations and the duration of storage of deposits in the reaction mixtures. The synthesis technique is described earlier [10,15,16,29] (*see also* Supplementary Material for experimental details). Noted that the chemical deposition of sulfides from aqueous solutions is a particular case of *one-pot* synthesis [30] which makes it possible to synthesize the nanoparticles directly in the aqueous medium. Deposited Ag_2S powders were washed with distilled water for removal of soluble impurity, filtered and dried in air at 323 K. Composition of the reaction mixtures and average particle size D of synthesized Ag_2S powders 1, 2, 3 and 4 are given in Table 1.

In situ high-temperature XRD (HT-XRD) experiments were performed using a X'Pert PRO MPD (Panalytical) diffractometer equipped with a position-sensitive fast sector detector PIXCEL and an Anton Paar HTK-1200 Oven furnace. HT-XRD patterns were recorded in the angle interval 2θ = 20–67.5° with a step of $\Delta(2\theta)$ = 0.026° and scanning time 200 s in each point. The diffraction measurements were performed at a temperature from 295 to 723 K with a step of ~25–30 K (*see also* Supplementary Material).

The synthesized silver sulfide samples were examined on a STADI-P (STOE) diffractometer in Cu$K\alpha_1$ radiation. X-ray measurements were performed in the angle interval 2θ = 20–95° with a step of $\Delta(2\theta)$ = 0.02° and large scanning time 10 s in each point. The resolution function $FWHM_R(2\theta) = (u\tan^2\theta + v\tan\theta + w)^{1/2}$ of a STADI-P (STOE) diffractometer was determined in a special diffraction experiment using the cubic lanthanum hexaboride LaB_6 (NIST Standart Reference Powder 660a) with lattice spacing a = 0.41569162 nm. The parameters of this resolution function $FWHM_R(2\theta)$ are u = 0.00616, v = −0.00457, and w = 0.00778.

The microstructure of the silver sulfide samples was studied by the scanning electron microscopy (SEM) method on a JEOL JSM 6390 LA microscope coupled with a JED 2300 Energy Dispersive X-ray Analyzer. Chemical composition of synthesized silver sulfide samples was estimated by EDX method. The contents of silver Ag and sulfur S in the synthesized coarse-crystalline (bulk) and nanocrystalline dried silver sulfide powders 1, 2, 3, and 4 are given in Table 1. The EDX spectra for all synthesized silver sulfide samples are shown in Fig. S1 (*see* Supplementary Material). The content of Ag and S in coarse-crystalline (bulk) powders 1 and 2 corresponds to stoichiometric sulfide Ag_2S. The content of silver Ag and sulfur S in the silver sulfide nanopowders 3 and