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Physical Chemistry Chemical Physics

Electronic Supplementary Information

High-Temperature X-ray Diffraction and Thermal Expansion of Nanocrystalline and Coarse-Crystalline Acanthite α-Ag_2S and Argentite β-Ag_2S

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Experimental details

Nanocrystalline powders of silver sulfide Ag_2S have been synthesized by chemical bath deposition from aqueous solution of silver nitrate $AgNO_3$ and sodium sulfide Na_2S with addition of a complexing agent. Sodium citrate $Na_3C_6H_5O_7 \equiv Na_3Cit$ was used as a complexing agent and electrostatic stabilizer. The initial solutions of $AgNO_3$, Na_2S, and Na_3Cit had equal concentrations, 500 mmol l^{-1}.

Synthesis was carried out in the following sequence. Complexing agent was added to 20 ml initial solution of silver nitrate while constant stirring. The volume of an added initial solution of sodium citrate Na_3Cit was varied from 2 to 40 ml. Then the distilled water was added and mixture volume was brought up to 190 ml. Resulting solution was mixed with 10 ml initial solution of Na_2S.

Deposition of silver sulfide occurred by the following reaction scheme

$$2AgNO_3 + Na_2S \xrightarrow{Na_3C_6H_5O_7} Ag_2S\downarrow + 2NaNO_3. \tag{1}$$

The concentrations of $AgNO_3$, Na_2S and Na_3Cit in all the reaction mixtures for the preparation of silver sulfide nanopowders were 50, 25 and 12.5 mmol l^{-1}, respectively.

When the solutions of reagents are mixed, silver sulfide is formed almost instantly; as a result, the reaction mixture first turns black, and then deposition of Ag_2S particles begins. The largest particles deposit during 1 h, the average-size (50-80 nm) particles agglomerate and also deposit. The deposition ends in one day, and the solution becomes transparent.

The upper part of colloid solution was decanted. Ag_2S powders deposited which remained after the decanting were washed with distilled water and dried in air at 323 K.

The coarse-crystalline Ag_2S powder was produced by hydrothermal synthesis from aqueous solutions of $AgNO_3$ and thiourea $(NH_2)_2CS$ with equal concentrations 50 mmol·l^{-1}. Thiourea $(NH_2)_2CS$ was used as a source of sulfur. The sulfide formation reaction took place in a closed vessel at 453 K for 4 h. The air and saturated vapor pressure over the solution was $\sim 1 \cdot 10^6$ Pa.

In situ high-temperature XRD (HT-XRD) experiments were performed using an X`Pert PRO MPD (Panalytical) diffractometer equipped with a Anton Paar HTK-1200 Oven furnace. HT-HRD patterns were recorded in the angle interval $2\theta = 20\text{-}67.5°$ with a step of $\Delta(2\theta) = 0.026°$ and scanning time 200 s in each point. X`Pert PRO MPD diffractometer was equipped with a position-sensitive fast sector detector PIXCEL, which simultaneously measures the intensity of reflection not at a separate point as an ordinary proportional counter, but in a 2θ range with a width of 3.154°. The use of this detector allowed one to reduce considerably the XRD pattern survey time with no compromise in quality. The diffraction measurements were performed at a temperature from 295 to 623 K with a step of ~25-30 K. When the assigned heating temperature was reached, the XRD pattern was recorded during 30 min.

All the deposited powders were examined by XRD method on a Shimadzu XRD-7000 and STADI-P (STOE) diffractometers in $CuK\alpha_1$ radiation. The XRD measurements were performed in the angle interval $2\theta = 20\text{-}95°$ with a step of $\Delta(2\theta) = 0.02°$ and scanning time of 10 sec in each point. The determination of the crystal lattice parameters and final refinement of the structure of synthesized silver sulfide powders were carried out with the use of the X'Pert Plus program package.[1] XRD pattern of monoclinic (space group $P2_1/c$) silver sulfide contains more than 100 diffraction reflections with different intensity in the range of 2θ angles from 20° to 95°.[2]

The average particle size D (to be more precise, the average size of coherent scattering regions (CSR)) in deposited silver sulfide powders was estimated by XRD method from the diffraction reflection broadening using the dependence of reduced reflection broadening $\beta^*(2\theta) = [\beta(2\theta)\cos\theta]/\lambda$ on the scattering vector $s = (2\sin\theta)/\lambda$.[3,4] According to,[3] the broadening of diffraction reflections is observed if particle size less than 100 nm. The value of broadening $\beta(2\theta)$ was determined by comparing the experimental width of each diffraction reflection, $FWHM_{exp}$, with the instrumental resolution function $FWHM_R$ of the X-ray diffractometer as $\beta(2\theta) = [(FWHM_{exp})^2 - (FWHM_R)^2]^{1/2}$. The resolution function $FWHM_R(2\theta) = (u\tan^2\theta + v\tan\theta + w)^{1/2}$ of the Shimadzu XRD-7000 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.

All the samples synthesized were characterized by XPS and UV-vis spectroscopy also.

The temperature and enthalpy of the acanthite – argentite phase transformation were determined by DTA-TGA method on a Setaram SETSYS Evolution 1750 thermal analyzer both during heating and during cooling. DTA and TGA experiments were carried out in argon Ar flow of 20 ml min^{-1} in the temperature range 293-493 K with a heating rate of 5 $K{\cdot}min^{-1}$ and during cooling from 493 K to 333 K with a cooling rate of 5 $K{\cdot}min^{-1}$.

Ag_2S nanopowders were studied using Raman scattering on Centaur U HR complex (NanoScanTechnology). As an example, the Raman spectrum of α-Ag_2S is shown in Fig. 3. Since the α-Ag_2S molecule is triatomic and non-linear, the bands are related to the symmetric stretching mode. The Raman spectrum of α-Ag_2S is characterized by intensive bands in the range of 90-300 cm^{-1}, in particular at 93, 188 and 243 cm^{-1} with a shoulder at 273 cm^{-1}.[5,6] Apart from the bands related to silver lattice vibrations (i.e. phonons) at 93 and 147 cm^{-1}, the others can be assigned to Ag-S-Ag symmetric stretching mode. A dominant sharp peak at ~430 cm^{-1} corresponds to low-temperature monoclinic α-Ag_2S phase.[7] Weak overtone and strong fundamental modes are detected at ~215 cm^{-1} and ~430 cm^{-1} correspond to the first-order and second-order longitudinal optical phonon modes in Ag_2S respectively and are the result of phonon vibration. Broadening of the peaks in the Raman spectrum indicate the formation of nanoparticles.

The microstructure and particle size of the silver sulfide powders and their elemental chemical composition 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. In addition, nanocrystalline silver sulfide was examined by transmission electron microscopy (TEM) method. The HRTEM images were recorded on a JEOL JEM-2010 transmission electron microscope with 140 pm (1.4 Å) lattice resolution. The elemental chemical composition of Ag_2S nanoparticles was studied on the same microscope with the use of an Phoenix (EDAX) Energy Dispersive Spectrometer with a Si(Li) detector having energy resolution of 130 eV. A copper grid with an aperture diameter of 50 μm was used for SEM and TEM observing of Ag_2S particles. One or two layers of collodium-glue (alcoholic solution of kolloksilin) were applied to Cu grid. After the drying of the glue coating, a carbon substrate with voids is formed. The Ag_2S powders to be examined were deposited on a carbon substrate. For studying Ag_2S nanoparticles we used such regions where the nanoparticles are located in the carbon substrate voids.

The average particle size D was estimated from the value of specific surface area S_{sp} also The specific surface area S_{sp} of the synthesized silver sulfide powders was found by the Brunauer-Emmett-Teller (BET) method from the isotherms of low-temperature adsorption of molecular nitrogen vapors at 77 K. The measurements were carried out by means of a Gemini VII 2390t Surface Area Analyzer. In the approximation that all particles have similar size and spherical shape, the average particle size D is equal to $6/\rho S_{sp}$ ($\rho = 7.25\ g{\cdot}cm^{-3}$ is the density of silver sulfide).

References

1 X'Pert Plus Version 1.0. Program for Crystallography and Rietveld analysis Philips Analytical B. V. © 1999 Koninklijke Philips Electronics N. V.

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SI Figures

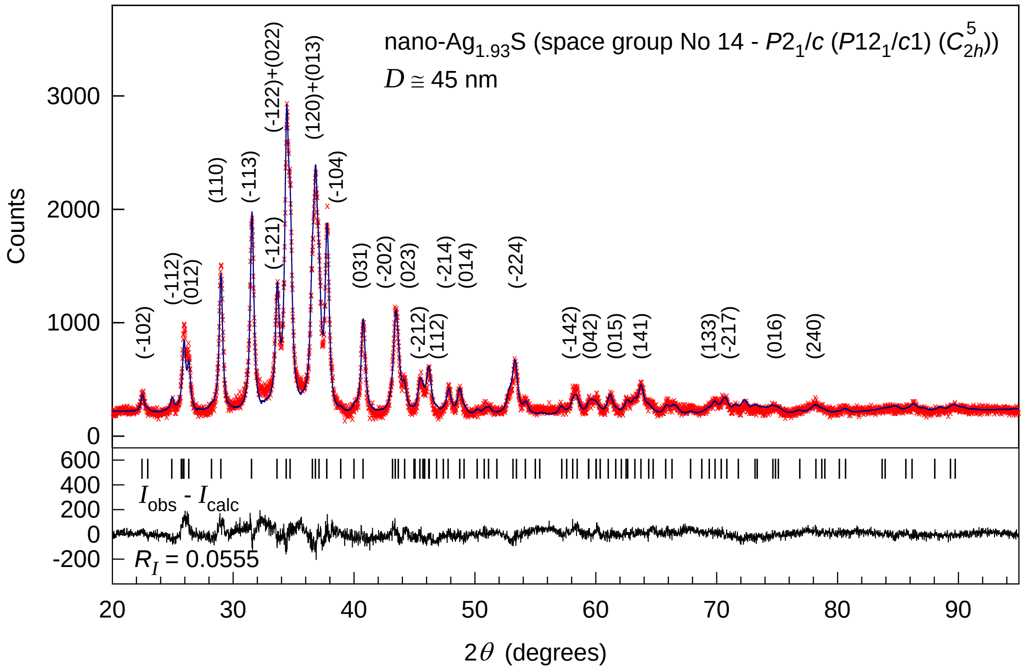

Figure S1. The experimental (×) and calculated (—) XRD patterns of deposited monoclinic Ag$_{1.93}$S nanopowder at a temperature of 295 K. The difference between the experimental and calculated XRD patterns ($I_{obs} - I_{calc}$) is shown in the lower part of the Figure. The XRD pattern is recorded in Cu$K\alpha_1$ radiation.

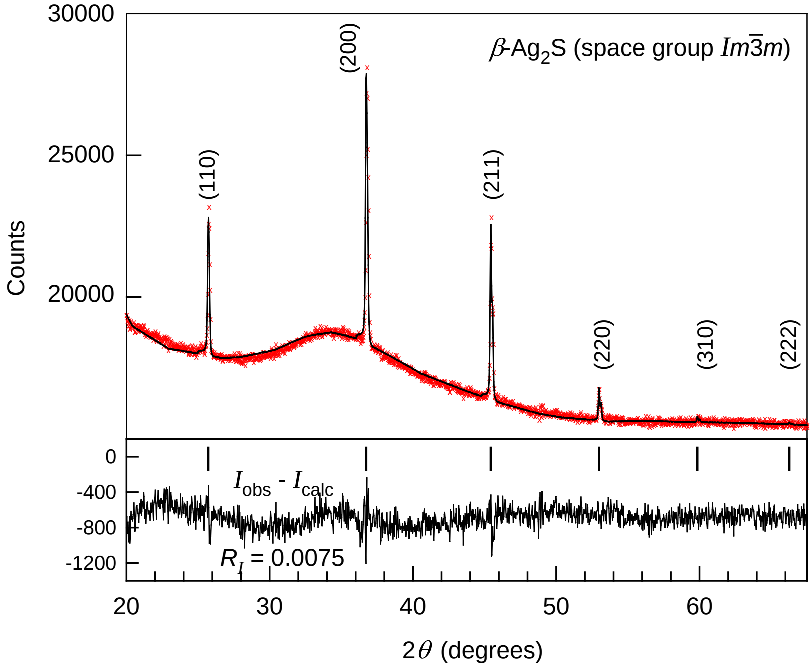

Figure S2. The experimental (×) and calculated (—) XRD patterns of bcc argentite Ag$_2$S at a temperature of 503 K. The difference between the experimental and calculated XRD patterns ($I_{obs} - I_{calc}$) is shown in the lower part of the Figure. The XRD pattern is recorded in Cu$K\alpha_1$ radiation.

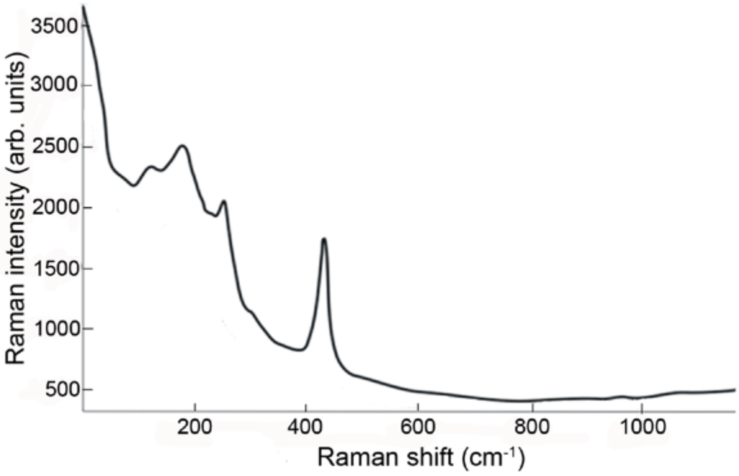

Figure S3. Raman spectrum of Ag_2S nanopowder.

SI Tables

Table S1. Refined crystal structure of coarse-crystalline monoclinic (space group No 14 - $P2_1/c$ ($P12_1/c1$) (C_{2h}^5)) silver sulfide Ag_2S with α-Ag_2S acanthite type structure at a temperature of 300 K: $Z = 4$, $a = 0.42264(2)$ nm, $b = 0.69282(3)$ nm, $c = 0.95317(3)$ nm, and $\beta = 125.554(2)^\circ$

Atom	Position and multiplicity	Occupancy	Atomic coordinates			$B_{iso}\times10^{-4}$ (pm^2)
			x	*y*	*z*	
Ag 1	4(*e*)	1.00	0.0715(7)	0.0151(3)	0.3094(3)	5.59(3)
Ag 2	4(*e*)	1.00	0.7264(7)	0.3241(4)	0.4375(3)	5.25(3)
S	4(*e*)	1.00	0.492(2)	0.234(1)	0.1321(7)	1.6800

Table S2. Refined crystal structure of monoclinic (space group No 14 - $P2_1/c$ ($P12_1/c1$)) $Ag_{1.93}S$ nanopowder at a temperature of 295 K: α-Ag_2S acanthite-type structure, $Z = 4$, $a = 423.4(3)$ pm, $b = 694.9(3)$ pm, $c = 954.9(5)$ pm, and $\beta = 125.43(6)^\circ$

Atom	Position and multiplicity	Atomic coordinates			Occupancy	$B_{iso}\times10^{-4}$ (pm^2)
		x	y	z		
Ag1	4(*e*)	0.0715(4)	0.0151(0)	0.3093(9)	0.97(1)	10.05(5)
Ag2	4(*e*)	0.7264(3)	0.3240(9)	0.4375(0)	0.96(4)	7.44(6)
S	4(*e*)	0.4920(2)	0.2339(8)	0.1321(1)	1.00(0)	1.96(0)

Table S3. Refined crystal structure of body centered cubic (space group No. 229 - $Im\bar{3}m$ ($I\,4m\bar{3}2/m$) (O_h^9))) silver sulfide with β-Ag_2S argentite-type structure at a temperature of 503 K: $Z = 2$, $a = b = c = 0.4874(1)$ nm

Atom	Position and multiplicity	Atomic coordinates			Occupancy	$B_{iso}\times10^{-4}$ (pm^2)
		x	y	z		
Ag1	6(*b*)	0	0.5	0.5	0.0978(7)	0.50
Ag2	48(*j*)	0	0.3306(5)	0.4122(7)	0.0711(0)	0.50
S	2(*a*)	0	0	0	1.00(0)	0.50