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Electronic Supplementary Information

Direct TEM observation of "acanthite α -Ag₂S - argentite β -Ag₂S" phase transition in silver sulfide nanoparticle

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Experimental details

Synthesis

Colloid solutions of Ag_2S nanoparticles and nanostructured powders of silver sulfide Ag_2S have been synthesized by chemical bath deposition from aqueous solution of silver nitrate $AgNO_3$, sodium sulfide Na_2S and sodium citrate $Na_3C_6H_5O_7 \equiv Na_3Cit$ with concentrations 50.0, 25.5 and 12.5 mmol·l⁻¹, respectively, at 298 K. Small excess of sodium sulfide Na_2S is necessary for synthesis of silver sulfide nanoparticles without an impurity of metallic Ag. Sodium citrate Na_3Cit was used as a complexing agent and electrostatic. All reagents with ACS highest purity were purchased by Sigma Aldrich and used without any further purification. All aqueous solutions have been prepared using high quality pure distilled deionized water. The initial aqueous solutions of $AgNO_3$, Na_2S , and Na_3Cit had equal concentrations, 500 mmol·l⁻¹.

Synthesis was carried out in the following sequence in dark. Complexing agent was added to 20 ml initial solution of silver nitrate under constant stirring. The volume of an added initial solution of sodium citrate Na₃Cit was varied from 2 to 40 ml. Then distilled deionized water was added and mixture volume was brought up to 190 ml. Resulting solution was mixed with 10 ml initial solution of Na₂S.

Deposition of silver sulfide occurred by the following reaction

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

The colloidal solutions above the deposited powders contain the finest nanoparticles. The upper part of colloidal solution was decanted (poured off) and was used for electron-microscopy study of Ag_2S nanoparticles contained therein. Deposited nanopowders which remained after the decanting (pouring off) were washed with distilled water and dried in air at 323 K.

Characterization

All the deposited nanopowders were examined by XRD method on a Shimadzu XRD-7000 diffractometer in $CuK\alpha_1$ radiation. The XRD measurements were performed in the angle interval $2\theta = 20-95^{\circ}$ with a step of $\Delta(2\theta) = 0.02^{\circ}$ and scanning time of 10 sec in each point. In situ hightemperature XRD (HT-XRD) experiments were performed in $CuK\alpha_1$ radiation using a X`Pert PRO MPD (Panalytical) diffractometer equipped with a Anton Paar HTK-1200 Oven furnace. HT-XRD patterns were recorded at a temperature from 295 to 623 K with a step of ~25-30 K in the angle interval $2\theta = 20-67^{\circ}$ with a step of $\Delta(2\theta) = 0.026^{\circ}$ and scanning time 200 s in each point. In addition, in situ high-temperature XRD study was carried out on a STADI-P (STOE) diffractometer in Debye-Scherrer geometry. The diffractometer was equipped with a quartz capillary furnace STOE. For better determination accuracy of lattice constants, measurements were performed in $CuK\alpha_1$ 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 diffraction measurements were carried out with the use of a linear position-sensitive detector while continuous rotation of the capillary with silver sulfide powder at a temperature from 295 to 773 K with a step of ~25-30 K. Qualitative and semi-quantitative phase composition of the powders was estimated using the Match! Version 1.10 software suite [1]. 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 HighScore Plus software package [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]. 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 LaB₆ (NIST Standart Reference Powder 660a) with lattice constant 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 Ag_2S colloid nanoparticles were examined by high-resolution transmission electron microscopy (HRTEM) method also. 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 nanostructured silver sulfide 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. For examination, colloidal solutions of Ag_2S nanoparticles were placed on a copper grid with collodium-glue covering. 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-containing grid with voids is formed.

The microstructure, size and elemental chemical composition of Ag₂S nanopowders were studied by the scanning electron microscopy (SEM) method on a JEOL-JSM LA 6390 microscope coupled with a JED 2300 Energy Dispersive X-ray Analyzer.

The size (hydrodynamic diameter) D_{dls} of the nanoparticles in the colloidal solutions was determined by non-invasive Dynamic Light Scattering (DLS) on a Zetasizer Nano ZS facility (Malvern Instruments Ltd) at 298 K. The He-Ne laser wavelength was 633 nm, the detection angle of back-scattering light was 173°.

Crystal structure of monoclinic (space group $P2_1/c$) nanocrystalline silver sulfide Ag_{1.93}S with α -Ag₂S acanthite-type structure (Table S1) refined in present study is in good agreement with the data [5]. Crystal structure of cubic (space group $Im\overline{3}m$) silver sulfide Ag₂S with β -Ag₂S argentite-type structure (Table S2) that also was refined in present study is in good agreement with the data [6, 7].

Temperature dependence of argentite lattice constant $a_{arg}(T)$ constructed on the generalised data of a high-temperature *in situ* XRD measurements in present study and works [7, 8] is shown in Figure S4. This $a_{arg}(T)$ dependence was used for an estimation of temperature of heating of Ag₂S nanoparticle.

References

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SI Tables

Table S1. Refined crystal structure of monoclinic (space group No 14 - $P2_1/c$ ($P12_1/c1$)) Ag_{1.93}S nanopowder with α -Ag₂S acanthite-type structure and particle size ~45-50 nm at 298 K [5, present study]: Z = 4, a = 0.4234(3) nm, b = 0.6949(3) nm, c = 0.9549(5) nm, and $\beta = 125.43(6)^{\circ}$

Atom	Position	Atomic coordinates			Occupancy	$B_{\rm iso} \times 10^{-4} (\rm pm^2)$
	and multiplicity	x/a	y/b	z/c		
Ag1	4(<i>e</i>)	0.0715	0.0151(0)	0.3093(9)	0.97	10.05(5)
Ag2	4(<i>e</i>)	0.7264	0.3240(9)	0.4375(0)	0.96	7.44(6)
			or			
		0.2736	0.8240(9)	0.0625(0)	0.96	7.44(6)
S	4(<i>e</i>)	0.4920	0.2339(8)	0.1321(1)	1.00	1.960

Table S2. Refined crystal structure of cubic (space group No. 229 - $Im\bar{3}m$ ($I4/m\bar{3}2/m$) (O_h^9)) silver sulfide Ag₂S with β -Ag₂S argentite-type structure at 463 K [present study] and 503 K [6, 7]: Z = 2, a = b = c = 0.4871(3) nm at 463 K, and a = b = c = 0.4874(1) nm at 503 K

Atom	Position and	Atomic coordinates			Occupancy	$B_{\rm iso} \times 10^{-4} (\rm pm^2)$
	multiplicity	x	у	Z.		
Ag1	6(<i>b</i>)	0	0.5	0.5	0.0978(7)	0.50
Ag2	48(<i>j</i>)	0	0.3306(5)	0.4122(7)	0.0711(0)	0.50
S	2(<i>a</i>)	0	0	0	1.00(0)	0.50

SI Figures



Figure S1. Evolution of XRD patterns of nanocrystalline acanthite α -Ag₂S with the average particle size of ~45-50 nm at heating from 300 to 433 K.



Figure S2. Evolution of XRD patterns of argentite β -Ag₂S in the temperature range 446-623 K. The inset shows a systematic displacement of the (200) diffraction reflection of bcc argentite with increase of measuring temperature.



Figure S3. The film strip plot of *in situ* high-temperature XRD data for Ag₂S nanopowder recorded in Debye-Scherrer geometry on air at a temperature from 298 to 773 K.



Figure S4. Dependence of the lattice constant a_{arg} of argentite β -Ag₂S on the temperature *T* measured by a high-temperature *in situ* XRD method. The approximation of measured lattice constant $a_{arg}(T)$ by the function (1) in the temperature range 448-723 K is shown by dotted line.



Figure S5. Scheme of displacement of S atoms from crystallographic positions of bcc argentite sublattice. and S atoms arrangement in monoclinic acanthite. Contours of undistorted cubic argentite lattice are shown by dashed lines. The argentite lattice, distorted because of displacement of S atoms is shown by solid line. Monoclinic (space group $P2_1/c$) unit cell of α -Ag₂S acanthite is shown by thick solid line. (1) is Ag atoms located inside monoclinic unit cell of acanthite α -Ag₂S, (2) and (3) are S atoms located inside and outside monoclinic unit cell, respectively.



Figure S6. Electron diffraction pattern obtained by FFT of HRTEM image of silver sulfide nanoparticle before radiation heating. The angles of 41.7°, 19.5°, and 29.1° between (010) and (011), (011) and (012), (012) and (001) diffraction spots of monoclinic α -Ag₂S acanthite are indicated.



Figure S7. Cumulative elemental EDS patterns of silver sulfide nanoparticle (*a*) before and (*b*) after electron beam heating.