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МОРФОЛОГИЯ И МАГНИТНЫЕ СВОЙСТВА НАНОЧАСТИЦЫ СУЛЬФИДОВ ЖЕЛЕЗА, СИНТЕЗИРОВАННЫХ МЕТОДОМ ТЕРМИЧЕСКОГО РАЗЛОЖЕНИЯ С РАЗЛИЧНЫМИ СУРФАКТАНТАМИ

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***Аннотация.** Исследованы морфология, магнитные и структурные свойства наночастиц сульфидов железа (Fe_xS_y), полученных методом термического разложения с использованием сурфактантов олеиламина, 1-гексадециламина и октадециламина. Наличие поверхностно-активного слоя подтверждается ИК-Фурье спектроскопией и термогравиметрическим анализом. Структурный анализ и мессбауэровская спектроскопия синтезированных наночастиц показали, что в случае сурфактантов ОЛА и ГДА основной фазой является Fe_3S_4 с включениями Fe_9S_{11} , и, значительная примесь FeS_2 , и даже Fe_2O_3 в случае ОДА сурфактанта. Отклонения распределения ионов железа по позициям в кристаллитах от распределения железа по позициям в монокристалле чистого грейгита и заметные изменения в спектрах магнитного кругового дихроизма (МКД) объясняются влиянием сурфактантов на процесс образования частиц, а также ролью границы между магнитным ядром и органической оболочкой.*

***Ключевые слова:** грейгит, термическое разложение, поверхностно-активные вещества, эффект Мессбауэра, ИК-Фурье спектры, магнитный круговой дихроизм, сульфиды железа.*

MORPHOLOGY AND MAGNETIC PROPERTIES OF IRON SULPHIDES NANOPARTICLES SYNTHESIZED BY THE THERMAL DECOMPOSITION METHOD WITH DIFFERENT SURFACTANTS

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Annotation. Morphology, magnetic, and structural properties were investigated of the iron sulphides (Fe_xS_y) nanoparticles fabricated by the thermal decomposition method using oleylamine, 1-hexadecylamine and octadecylamine surfactants. The presence of surfactant layer is confirmed by FT-IR spectroscopy and thermo-gravimetric analysis. The structural analysis and Mössbauer spectroscopy of synthesized nanoparticles showed in main Fe_3S_4 phase with inclusions of Fe_9S_{11} in cases of OLA and HDA surfactants and significant admixture of FeS_2 and even Fe_2O_3 in case of ODA surfactant. Deviations of iron ions distribution among crystal positions from that in bulk pure greigite and the pronounce changes in the magnetic circular dichroism (MCD) spectra are explained with the influence of surfactants on the particles formation process as well with the role of the boundary between magnetic core and organic shell.

Keywords: greigite, thermal decomposition, surfactants, Mössbauer effect, FT-IR spectra, magnetic circular dichroism, iron sulphides

An increasing interest in chalcogenide nanoparticles (NPs), in particular, iron sulfides NPs is due to the transition from the ionic character of bonds in the widely studied and applied iron oxides to the covalent character in the chalcogenides which leads to an appearance of transport and optical properties, similar to those of semiconductors or even metals, and the emergence of new fields of application.

The chemical and phase composition, magnetic properties, and possibilities of practical applications of NPs can be controlled by synthesis methods. One of the most frequently used is the thermal decomposition method [1], the advantages of which are the simplicity of the experiment, mild conditions, and a relatively short reaction time. In this case, it is possible to use surfactants that perform a double function: controlling the growth of particles and preventing their aggregation. Many researchers have used surfactants to control the properties of the magnetite NPs (e.g., [2]). For iron sulfide NPs, such studies are just beginning; in particular, we recently published the first results of studying the effect of surfactants on the Mössbauer and magneto-optical spectra of greigite NPs [3]. This work is devoted to the in-depth study of the effect of three different amines on the morphology, phase composition, and magnetic properties of iron sulfide (Fe_xS_y) NPs.

NPs were synthesized with the thermal decomposition of the mixture of complexes of the fatty amines: oleylamine, $C_{18}H_{35}NH_2$, – sample OLA, 1-hexadecylamine, $C_{16}H_{35}N$, – sample HDA and octadecylamine, $C_{18}H_{39}N$, with iron nitrate, $(Fe(NO_3)_3 \cdot 9H_2O)$, sulfur powder, and oleic acid (OA). OLA, HDA and ODA being kinds of alkyl-amines were used here as surfactants, oleic acid provided more rapid kinetics. The reaction parameters used in the synthesis of a series of iron sulfide NPs are listed in (Tab. 1).

Table 1. The brief description of the synthesis process and phase composition according to the Mössbauer effect

Sample name	Synthesis description	Phase composition
Fe ₃ S ₄ -OLA)*	S-powder+Fe(NO ₃) ₃ ·9H ₂ O+OLA+OA (240 °C, 30min.)	Fe ₃ S ₄ + ~2% Fe ₉ S ₁₁
Fe ₃ S ₄ -HDA	S-powder+Fe(NO ₃) ₃ ·9H ₂ O+HDA+OA (240 °C, 30min.)	Fe ₃ S ₄ + ~5% Fe ₉ S ₁₁
Fe ₃ S ₄ -ODA	S-powder+Fe(NO ₃) ₃ ·9H ₂ O+ODA+OA (240 °C, 30min.)	Fe ₃ S ₄ + ~33% FeS ₂ + ~45% Fe ₂ O ₃

*) The formula is used here and hereinafter only for designation of samples.

Morphology of the synthesized NPs was examined using a JEM-2100 transmission electron microscope (JEOL Ltd.) operating at an accelerating voltage of 200 kV. Selected-area electron diffraction (SAED) was used to determine the structure of separate NPs. Fourier transform infrared absorption (FT-IR) spectra were recorded with the VERTEX 70 (Bruker Optic GMBH) spectrometer in the spectral region of 400 ÷ 4000 cm⁻¹ with spectral resolution 4 cm⁻¹. To obtain FT-IR spectra, a transparent tablets were prepared by pressing a mixture of powders of KBr and of nanoparticles with a concentration 0.7%. The differential Scanning Calorimeter DSC 204 F-1 Phoenix (NETZSCH) was used to estimate the strength of the surfactants bonding with the magnetic core. The Mössbauer effect spectra of the samples were obtained on an MS-1104Em spectrometer in transmission geometry with a ⁵⁷Co (Rh) radiation source at 300 K. Magnetic properties of the samples were studied using MCD in energy range 1.25–3.5 eV in a magnetic field of 1.3 T at a temperature of 300 K in transmitted light on the transparent containing NPs composite plates made in a special way in weight ratio of NPs to silicon as the 0.5 / 100 [3,4]. The measurement accuracy was about 10⁻⁴, and the spectral resolution was 20–50 cm⁻¹, depending on the wavelength.

For all samples, NPs observed with electron microscope were of different shapes - mainly regular hexagons and parts of hexagons and with a large size distribution (Fig. 1). Absence of contact between neighboring NPs (for example, Fig. 1b) may indicate the presence of an organic NPs coating. SAED patterns confirmed good NPs crystallinity, and the crystal structure of larger NPs belonging to the Fe₃S₄ of Fd-3m space group but admixtures of sulfur compounds with the higher S content could not be excluded in smaller NPs.

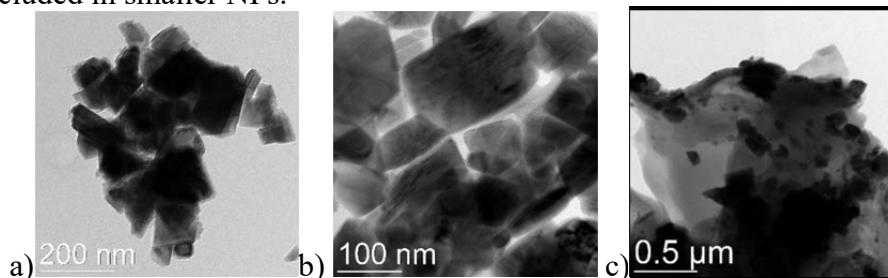


Fig. 1. TEM images in different scales of the Fe₃S₄-OLA (a), Fe₃S₄-HDA and Fe₃S₄-ODA (c) NPs.

Presence of the coating organic layers on nanoparticles was confirmed by DTA and the FT-IR spectra analysis of all three samples in comparison with FT-IR spectra of uncoated Fe₃S₄ NPs and pure OLA, ODA and HDA surfactants. In all FT-IR spectra, bands are observed characteristic of C-S chemical bonds of organic shell with crystal core of samples. The DTA results showed the stability of the core structure of all samples up to 850 °C. The weight losses upon heating indicated that the organic coatings of the magnetic core is much thicker in the HDA and ODA samples as compared to the OLA sample, which agrees with the electron-microscope image. After heating during DTA experiments for Fe₃S₄-HAD and Fe₃S₄-OLA samples the FT-IR spectra became similar to the FT-IR spectrum of uncoated Fe₃S₄ NPs. Judging by the weight loss upon heating, the organic coating on the magnetic core is much thicker in the ODA sample as compared to the HDA and in the HDA sample comparing to the OLA, which agrees with the electron-microscope images.

Mossbauer spectra analysis revealed a superparamagnetic state at room temperature of about one third of the nanoparticles both for Fe₃S₄-OLA and Fe₃S₄-HDA and three quarters for Fe₃S₄-ODA. In this last case, doublet in the Mossbauer spectrum characteristic of superparamagnetism is preserved even at 4.2 K though less intense. Besides, Mossbauer spectra revealed deviations in the distribution of Fe³⁺ and Fe²⁺ ions over crystal positions from that in the inverted spinel in which greigite belongs. The population of the tetrahedral positions of the inverted spinel, in our case Fe₃S₄, should be half of that of the octahedral ones, which is not observed in the present samples. At

that, a deficiency of iron ions in A positions are observed for sample Fe_3S_4 -OLA and Fe_3S_4 -ODA while for Fe_3S_4 -HDA sample there are not enough ions in the B positions. It is assumed that different chemical activity and different degree of unsaturation of the surfactant molecules effects on the properties of the NPs magnetic core in the course of its formation.

In Fig. 3, MCD spectra are shown for all samples together with spectrum of the greigite NPs synthesized earlier with polyol mediated process. All three spectra are close to each other in shape; the energy of maximum near 2 eV stays, practically, unchanged, while the point of the MCD curve intersection with the energy axis shifts differently to higher energies. The shifts are evidently stronger for the HDA sample, even a new negative peak near 1.3-1.4 eV becomes apparent for this sample. These changes can be explained by the influence of types of coatings on the Fe ions distribution between octahedral and tetrahedral crystal positions. This can lead to some changes in the density of states and, consequently, to the observed shift of bands in the MCD spectrum and a redistribution of the maxima intensities.

Summarizing the results of the work. Differential thermal analysis revealed a different percentage of the surfactants absorbed on the particles surface. The major weight loss was observed for the octadecylamine. FTIR spectra suggested the coordination of the different surfactant to the surface of the synthesized nanoparticles. Mössbauer data indicated close to the single phase, Fe_3S_4 , composition for OLA and HDA surfactants while several phases Fe_3S_4 , FeS_2 , and even Fe_2O_3 coexisted in particles forming with ODA. Only for the OLA sample, MCD spectrum (extremely sensitive to a sample phase composition) coincides with that of the Fe_3S_4 NPs synthesized with the polyol mediated process [3]. For the HDA sample the redistribution of the spectral maximum intensities and the whole spectrum shift to higher energies are observed. In the case of ODA, the MCD signal decreases dramatically. Thus, all three types of surfactants used ensure the formation of an organic shell chemically bound to the magnetic core of the particle, but only in the case of OLA, the magnetic core of the particle is single-phase.

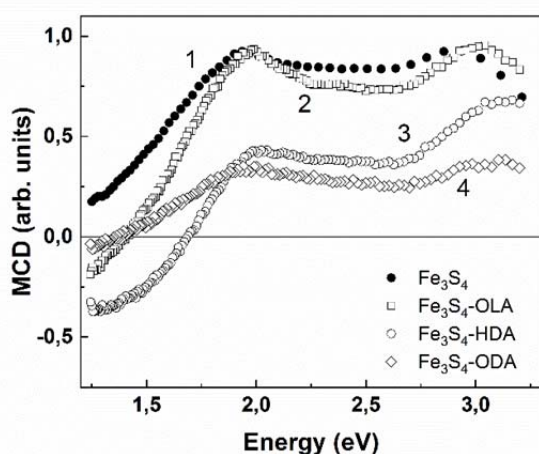


Fig. 2. Room temperature MCD spectra for the Fe_3S_4 NPs, synthesized with the polyol mediated process without surfactants (1), the OLA (2), the HDA (3) and ODA (4) samples in magnetic field 5.0 kOe.

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