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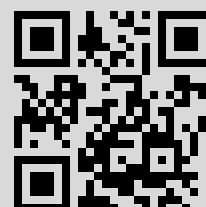
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Structure and Magnetic Properties of Biogenic Ferrihydrite Nanoparticles Doped with Gadolinium

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Bacterial culture Klebsiella oxytoca was grown in a Lovley medium at various concentrations of gadolinium salt. Biogenic magnetic nanoparticles of ferrihydrite were investigated by Mossbauer spectroscopy and magnetization curves were obtained. The results of structural studies showed that iron Fe(5) takes new position when cultivating is carried out in medium with high concentrations of gadolinium. It was found that gadolinium is fit into the crystal structure of ferrihydrite. These results are consistent with the analysis of the magnetization curves.

Keywords: ferrihydrite nanoparticle, bacterial culture Klebsiella oxytoca, Mössbauer spectroscopy, gadolinium doping.

Introduction

In recent decades, a considerable interest in nanomaterials has been expressed. This is due to their unique physical and chemical properties. Iron oxide nanoparticles have attracted considerable attention, because of their application in various fields of science and technology. It was proved that hematite ($\gamma - Fe_2O_3$) nanomaterials, the most stable form of iron oxide in the environment, can be used as gas sensors, catalysts [1] and electrode materials [2]. Potential applications of iron oxide magnetic nanoparticles (Fe_3O_4 and Fe_2O_3) in biomedicine, as a contrast

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agent for magnetic resonance imaging (MRI), in treating hyperthermia, for medicine delivery and in magnetic separation of biological objects are very promising [3].

To use magnetic nanoparticles in biomedical applications they should meet the following requirements: 1) the dispersion of nanoparticles sizes is small and their hydrodynamic diameter should be less than 50nm, 2) nanoparticles should be superparamagnetic particles [2], 3) they must be biocompatible and, 4) nanoparticles must be stable in aqueous solutions it ensures their transport in biological tissues.

To prepare nanoparticles with desired characteristics various methods are used, for example, heat treatment and doping of nanoparticles with other metals. Such procedures change nanoparticles composition and result in phase and structure transitions [4–6]. Substitution of iron in ferrites by gadolinium, zinc, manganese and nickel results in change in the Curie temperature, in the rate of heating in an alternating magnetic field and in the magnitude of specific saturation magnetization [7–9]. So these nanoparticles can be used for the local magnetic hyperthermia because the Curie temperature is close to the temperature of the human body. Biocompatible nanoparticles that can be heated up to 43 – 45°C may be applied in cancer therapy. They can destroy tumor cells in alternating magnetic field without damaging healthy tissue. Nanoparticles of ferrite doped by gadolinium ions are being studied extensively for possible application as contrast agents in magnetic resonance imaging (MRI). The iron ions are much less toxic than gadolinium ions and iron ions can be reused by cells using normal biochemical pathways for iron metabolism [7, 8]. Gadolinium compounds are used in cancer therapy based on the neutron capture technique.

In industrial microbiology and geochemistry microorganisms are well known for their ability to mineralize high specific amount of iron under anaerobic conditions, in particular, they are able to accumulate ferrihydrite. Bacterial culture *Klebsiella oxytoca* grows well in laboratory conditions so it can be used as "biofactory" for the nanoparticles production. In this paper, we report the results of structural and magnetic investigations of biomineral ferrihydrite nanoparticles doped with gadolinium ions. Such nanoparticles (radius $R = 4,87 \pm 0,02 \text{ nm}$ and height $L = 2,12 \pm 0,04 \text{ nm}$) have the biocompatible shells. They are able to absorb drugs on their surfaces and are stable in aqueous solutions [10, 11]. All these characteristics allow us significantly broad the area of possible applications of biogenic ferrihydrite nanoparticles.

1. Experimental procedure

The microorganisms *Klebsiella oxytoca* used in this study were isolated from sapropel found in Borovoe Lake (Krasnoyarsk region). The sapropel was passed through a magnetic separator. The isolated microorganisms were inoculated onto an agarized Lovley medium and cultured under anaerobic conditions to obtain colonies. The biomass grown in the liquid medium was checked for the presence of magnetic particles with the use of FMR spectrometer. In this study, the bacterial biomass have been grown under microaerophilic conditions on a Lovley medium of the following composition (g/l): $NaHCO_3 - 2.5$, $CaCl_2 \bullet H_2O - 0.1$, $KCl - 0.1$, $NH_4Cl - 1.5$, $NaH_2PO_4 \bullet H_2O - 0.6$, ferric citrate (concentration of ions Fe^{3+} is 0.114), 6% solution of potassium citrate – 5 ml, yeast extract concentration was 0.05, benzoic acid concentration was varied from 0.2 to 0.5 [12]. Gadolinium salt $Gd_2(CO_3)_3$ was added to the culture medium with the following concentrations: 0.0114 g/l, 0.057 g/l and 0.114 g/l. Bacterial biomass was separated from nanoparticles by centrifugation (10 min at 10000 rpm) and then it was destroyed with ultrasonic disintegrator UZDN (1 min, 44 kHz, 20 W). The obtained powder was dried at temperature $T = 40 - 80^\circ C$.

The measurements of Mössbauer spectra were carried out using a $Co_{57}(Cr)$ source with a line width at half height of 0.24 mm/s for a sodium nitroprusside powder absorber. The thickness of the samples under investigation was equal to 5 – 10 mg/cm^2 according to the natural iron content

for which the intensities of spectral lines are linearly related to the iron content in the phase. Mössbauer spectra were measured at room temperature. The spectra were analyzed in two stages. At the first stage, the probability distribution functions of the quadrupole splittings $P(QS)$ were determined. The peaks positions define the number and values of the parameters of the hyperfine structure of iron positions. In the second stage, the model spectrum was constructed and then it was fitted to the experimental data by varying the entire set of hyperfine structure parameters.

The Mossbauer spectroscopy was previously used to identify the magnetic structure of ferrihydrite. It was revealed that there are four nonequivalent positions of iron ions with the relatively small distortions of isomeric chemical shifts and different quadrupole splittings: $QS(Fe(1)) \sim 0.5$ mm/s and $QS(Fe(2)) \sim 1$ mm/s. Positions with a high degree of distortion were also found. They are $QS(Fe(34)) (1.5-1.8)$ mm/s [13].

The defective phase of ferrihydrite consists of a random sequence of defective blocks: d-ABA and d-ACA [14]. Two neighboring defective layers in the stacking sequence d-ABAC form a double-layer occupied by octahedra (Fig. 1). A combination of defective layers with the stacking sequence d-ABAB or d-ACAC gives a single layer of Fe-occupied octahedra in the ferrihydrite structure, as shown in Fig. 2.

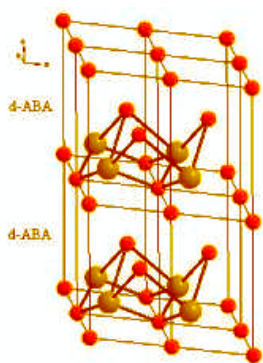


Fig. 2. Schematic representation of Fe–O–Fe bonds in the defective phase ABABA by notation in Jansen et al. [14]; small circles represent O and OH ligands, and large circles represent Fe^{3+} ions

can be identified with the positions of double and single layers, respectively. Breaking the bonds to neighboring octahedra also contributes to local distortion. The equal occupancy of Fe(3) and Fe(4) sites suggest that ferrihydrite nanoparticles contain single and double ligand octahedra occupied by Fe.

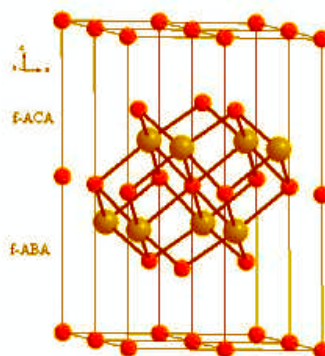


Fig. 1. Schematic representation of Fe–O–Fe bonds in the defect-free phase ABACA by notation in Jansen et al. [14]; small circles represent O and OH ligands; large circles represent Fe^{3+} ions

Each oxygen octahedron of a single layer has three Fe–O bonds with the length equals 1.87 Å and three bonds with the length equals 2.32 Å. Each oxygen octahedron has also trigonal distortion and this distortion is far stronger in comparison with the octahedral distortion in double-layers. The ABABACAC sequence of ligand layers results in equal occupancy of the octahedra in single and double-layers. Thus, the structure of ferrihydrite allows the existence of two nonequivalent positions of iron populated with a 1:1 ratio at a specific ordering of ligand layers.

In terms of the idealized structural model given above the Fe(1) and Fe(2) positions in the bacterial ferrihydrite

2. Results and discussion

Mössbauer spectra of the nanoparticles doped with gadolinium is represented by superposition of several quadrupole doublets.

The probability distribution of the quadrupole splitting (Fig. 3) shows that new iron positions occur in ferrihydrite produced by the bacteria with increasing concentration of gadolinium in Lovley medium. This results in various degree distortions in the local environment.

Fitting the model spectrum of quadrupole splitting P(QS) to the experimental spectrum gives the parameters of hyperfine structure of the spectra. The parameters values are presented in Tab. 1. The following identification of the iron positions is used: Fe(1) is the iron atom in double layer, Fe(2) is the iron atom in a single layer, Fe(3) are the iron atoms that enter the layer of empty octahedra. This results in the structure that consists of octahedra connected along the *c*-axis. Such structure is characteristic of the hematite structure.

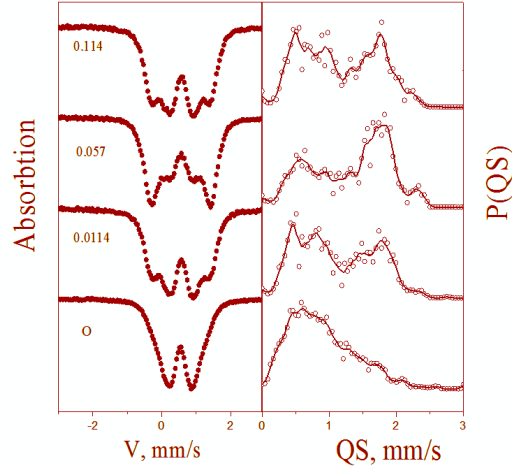


Fig. 3. Mössbauer spectra and probabilities of the quadrupole splitting of the biogenic ferrihydrite at different gadolinium concentrations in Lovley medium

Table 1. Hyperfine structure parameters of Mössbauer spectra for biomass *Klebsiella oxytoca*

Lovley medium with different concentration of gadolinium, g/l	IS	QS	W	S	Position
o	0.391	0.50	0.35	0.39	Fe(1)
	0.384	0.92	0.40	0.42	Fe(2)
	0.383	1.51	0.41	0.19	Fe(3)
Gd 0.0114	0.420	0.50	0.36	0.29	Fe(1)
	0.408	0.91	0.41	0.31	Fe(2)
	0.398	1.53	0.37	0.24	Fe(3)
	0.399	1.90	0.31	0.16	Fe(4)
Gd 0.057	0.409	0.56	0.40	0.28	Fe(1)
	0.398	1.06	0.41	0.19	Fe(2)
	0.408	1.56	0.31	0.24	Fe(3)
	0.401	1.86	0.28	0.24	Fe(4)
	0.389	2.26	0.24	0.05	Fe(5)
Gd 0.114	0.416	0.54	0.38	0.36	Fe(1)
	0.404	0.96	0.35	0.23	Fe(2)
	0.404	1.34	0.28	0.09	Fe(3a)
	0.404	1.61	0.25	0.14	Fe(3b)
	0.404	1.87	0.23	0.12	Fe(4)
	0.410	2.18	0.26	0.06	Fe(5)

Fig. 4 shows that the proportion of iron in positions Fe (1) and Fe (2) is decreased for bacterial ferrihydrite synthesized with gadolinium concentration 0.0114 g/l in the culture medium. On the other hand, the proportion of iron in position Fe (3) is increased and new positions Fe (4) came into existence. This result is easily explained if we assume that gadolinium atoms occupy empty octahedral layers of ferrihydrite. The relatively large ionic radius of gadolinium results in distortion of faces of adjacent octahedra occupied with iron atoms.

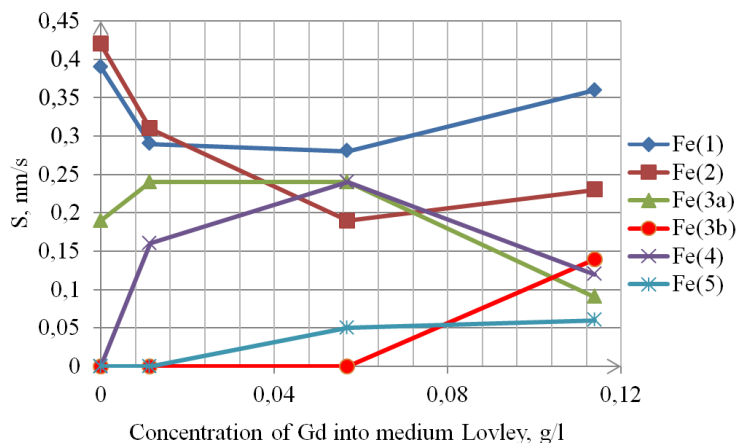


Fig. 4. Fractional occupancy of the Fe^{3+} ion positions in ferrihydrite as a function of the gadolinium concentration

The iron atoms in octahedra which are adjacent to gadolinium octahedron, were taken as the iron positions Fe (4). The embedding of gadolinium into ferrihydrite results in expansion of the lattice. The lattice expansion causes an increase in the isomer chemical shift for all ferrihydrite positions (see Fig. 5) or a decrease in the electron density at the iron nuclei. Thus gadolinium atoms improve the transfer of adjacent iron atoms from double and single layers in the position Fe (4). This promotes formation of hematitic positions and leads to increase of occupancy of the position Fe (3).

When gadolinium concentration in the medium is increased to 0.057 g/l the occupancy of iron positions Fe (1) in double layers and hematitic positions Fe (3) does not change. It means that gadolinium atoms do not enter the interlayer positions. This is because the positive charge density of cations is higher in comparison with the negative charge density of anions and proportion of positions Fe (2) of single layers of iron is reduced. Gadolinium atoms enter the single layers of octahedra, displace the iron atoms and create new positions Fe (5). This decreases the occupancy of Fe (1) positions as shown in Fig. 5. An increase in the occupancy of Fe (1) and Fe (2) positions, and reduction of iron positions Fe (4) is observed as gadolinium concentration grows to 0.114 g/l (see Fig. 3). It is likely that gadolinium atoms are displaced from the structure of ferrihydrite to form a new crystallographic phase on the basis of single layers. Hematitic positions Fe (3) can be divided into two groups: positions with small quadrupole splitting and positions with large quadrupole splitting. This is due to the different number of adjacent gadolinium atoms.

The magnetization curves $M(H)$ and temperature dependence of magnetization were measured using a vibration magnetometer with a superconducting solenoid. Fig. 6 shows magnetization curves of biogenic ferrihydrite synthesized with different concentrations of gadolinium salt in the growth medium for microorganisms. Measurements were carried out at 4,2 K.

When the result shown in Fig. 6 is compared with the temperature dependence of magnetization of ferrihydrite, it is apparent that the magnetic properties of ferrihydrite nanoparticles are

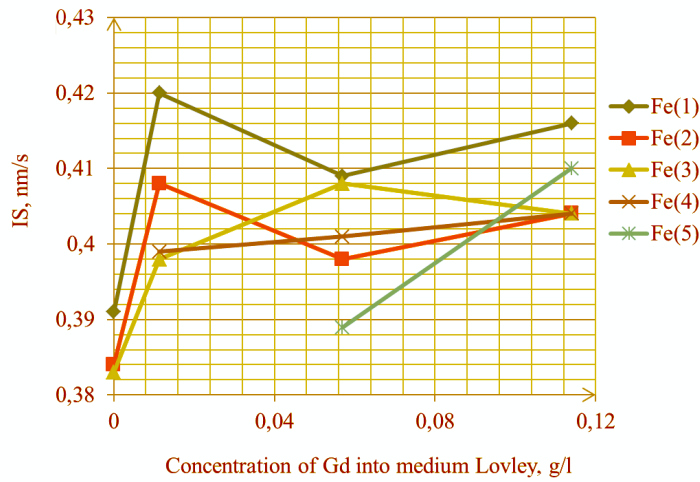


Fig. 5. IS - isomer chemical shift of nonequivalent iron positions relative to α -Fe in the bacterial ferrihydrite as a function of gadolinium concentration in the Lovley medium

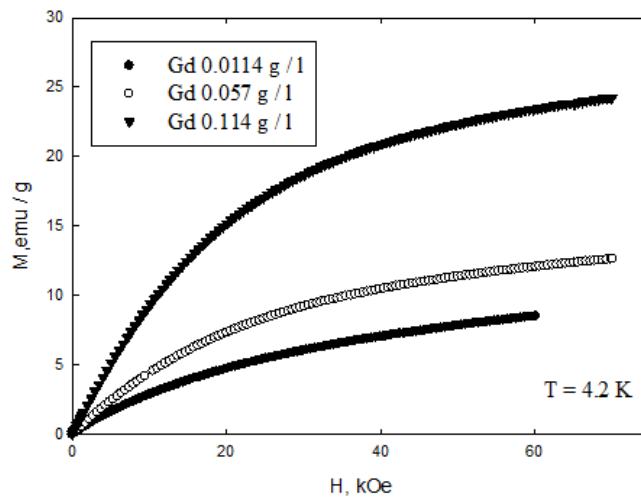


Fig. 6. The magnetization curves of ferrihydrite synthesized with different concentrations of gadolinium salt in the bacterial Lovley medium

changed substantially with the presence of gadolinium salt in the culture medium. This means that gadolinium atoms are involved in the bacterial metabolism and magnetic nanoparticles containing gadolinium atoms are produced.

Conclusions

Analysis of the Mossbauer spectra results shows the new positions of iron Fe (5) when microorganisms are cultured in the medium with high concentrations of gadolinium salt. One can assume that gadolinium atoms are embedded in the crystal structure of ferrihydrite. Analysis of the magnetization curves supports this assumption.

Acknowledgments

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Структура и магнитные свойства биогенных наночастиц ферригидрита, легированных гадолинием

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*Бактериальная культура *Klebsiella oxytoca* была выращена на среде Lovley с добавлением соли гадолиния в различных концентрациях. Биогенные магнитные наночастицы ферригидрита исследованы методом Мёссбауэра, и получены кривые намагничивания. Результаты структурных исследований показывают новую позицию железа Fe(5) при культивировании в среде, содержащей более высокие концентрации гадолиния. Следовательно, Gd встраивается в кристаллическую структуру ферригидрита. Эти результаты согласуются с результатами анализа кривых намагничивания.*

*Ключевые слова: наночастицы ферригидрита, бактериальная культура *Klebsiella oxytoca*, мёссбауэровская спектроскопия, легирование гадолинием.*