

SATURATION MAGNETIZATION AND PHASE COMPOSITION OF SYNTHESIZED MAGNETIC NANOPARTICLES

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ABSTRACT

The organisms of different animals, including human beings contain magnetite nanoparticles. Creation of synthetic analogues of this biomineral is of great importance for solving of wide range of scientific problems. We describe here the creation and investigation of synthetic magnetic nanoparticles. Four samples of magnetic nanoparticles were synthesized by the method of co-precipitation of iron salts at ambient temperature with and without ultrasonic treatment. The characterization of synthesized magnetic nanoparticles was performed by Nuclear Gamma Resonance (NGR) and magnetometry. It was shown, that application of ultrasonic treatment during the synthesis of magnetic nanoparticles leads to formation of superparamagnetic nanoparticles. In our opinion it takes place due to formation of single superparamagnetic nanoparticles during the covering procedure. If covering procedure takes place in the absence of ultrasonic treatment, aggregation of uncovered nanoparticles happened and formation of aggregated magnetite nanoparticles, covered by silica occurs.

Key words: magnetic nanoparticles, superparamagnetic properties

INTRODUCTION

Research of properties of biogenic magnetite and its synthetic analogues is of great importance for solution of a wide range of mineralogical, medicobiological and material science problems. Biogenic magnetite is the most intriguing biomineral. It is believed, that biogenic magnetite serve for realization of a wide range of biological functions, including realization of the animals' orientation in the space [1] and play an important role in the brain functioning. Magnetite is ferrimagnetic at ambient temperature. Biogenic magnetite is nearly perfect single crystals without defects and dislocations [2]. The size of such crystals is usually in a range from 10 to 200 nm and they are tending to be rather pure iron oxides. It is known, that biogenic magnetite has unique magnetic properties [3]. In our laboratory by means of magnetic resonance the room-temperature macroscopic quantum oscillations in nanobiomagnetite of brain tissues have been discovered. When the microwave power exceeds a critical

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value, the coherent signals are appearing on the contour of the resonance lines. The increase of the power leads to increasing the quantity of the coherent signals, which characterize the quantum oscillations in the nanoscale particles. The resonance characteristics of such nanobiomagnetite differ essentially from other materials, namely, no one from other known natural or synthetic materials shows room-temperature macroscopic quantum oscillations.

During last two decades many different methods of magnetic nanoparticles synthesis were developed [4]. Among them: microemulsions, sol-gel syntheses, sonochemical reactions, hydrothermal reactions, hydrolysis and thermolysis of precursors, flow injection and electrospray syntheses. But the most widespread, simplest and most efficient method for magnetic nanoparticles synthesis is the method of iron salts co-precipitation, although huge variety of reaction parameters have an influence upon the properties of obtained nanoparticles (phase composition, size, magnetic characteristics etc.). Among them pH, ionic strength, temperature, nature of the salts (perchlorates, chlorides, sulfates, and nitrates), iron salts concentration ratio. It is very important to study the influence of these parameters upon the characteristics of synthesized magnetic nanoparticles.

Many factors can define magnetic properties of synthesized magnetic nanoparticles; among them one can mention chemical composition of the nanoparticles, crystal lattice type, degree of crystal lattice imperfection, size and shape of the particles, interaction of nanoparticles with surrounding matrix and adjacent particles [5]. By changing of the size, shape, composition and structure of nanoparticles, one could in some degree manage magnetic characteristics of such materials. It is very difficult to control all these factors during the synthesis of nanoparticles with roughly same size and chemical composition, that's why the properties of single-type materials could vary greatly.

We report here the method of magnetic nanoparticles preparation and investigation of their magnetic properties by the methods of magnetometry and NGR.

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

All chemicals and solvents used were of analytical grade and used without further purification. The water was the reagent-grade. All solutions were freshly prepared. All samples were synthesized by the co-precipitation method. *Sample M1* was synthesized by co-precipitation of 4.0 ml of 1M iron (III) chloride solution and 1 ml of 1M iron (II) sulfate solution by 1M NH_4OH (reaction time is 40 min). The obtained nanoparticles were covered by 4% (3-aminopropyl) triethoxysilane that was adsorbed onto the surface of the magnetic nanoparticles at 90°C for 2,5 hours at mild ultrasonic treatment. The resultant product was thoroughly rinsed with 0,05 M KOH, deionised water and ethanol to remove the residual surfactant and unreacted reagents. *Sample M2* was synthesized by co-

precipitation of 4.0 ml of 1M iron (III) chloride solution and 1 ml of 2M iron (II) sulfate solution by 1M NH_4OH (reaction time is 14 min). The obtained nanoparticles were covered by 4% (3-aminopropyl)triethoxysilane that was adsorbed onto the surface of the magnetic nanoparticles at 90°C for 2,5 hours at mild ultrasonic treatment. The resultant product was thoroughly rinsed with 0,05 M KOH, deionised water and ethanol to remove the residual surfactant and unreacted reagents. *Sample M3* was synthesized by co-precipitation of 4.0 ml of 2M iron (III) chloride solution and 1 ml of 1M iron (II) sulfate solution by 1M NH_4OH (reaction time is 26 min). The obtained nanoparticles were covered by 4% (3-aminopropyl)triethoxysilane that was adsorbed onto the surface of the magnetic nanoparticles at 90°C for 2,5 hours at mild ultrasonic treatment. The resultant product was thoroughly rinsed with 0,05 M KOH, deionised water and ethanol to remove the residual surfactant and unreacted reagents. *Sample Mag50* was synthesized by co-precipitation of 4.0 ml of 1M iron (III) chloride solution and 1 ml of 2M iron (II) sulfate solution by 1M NH_4OH . Obtained magnetite was coated with silica via tetraethoxysilane hydrolyzation in alcohol-water-ammonia mixture. Thereto, 100 ml of ethanol, 2 ml of concentrated NH_4OH were added to the reaction mixture at slow mechanical stirring. After that, 3 ml of tetraethoxysilane (TEOS, 98% (v/v)) were added drop-by-drop to the reaction mixture. The hydrolysis of TEOS was carried out for 20 hours under normal conditions. The resultant product was thoroughly rinsed with 0,05 M KOH, deionised water and ethanol to remove the residual surfactant and unreacted reagents.

The properties of synthesized magnetic nanoparticles were analyzed by the methods of NGR and magnetometry.

RESULTS AND DISCUSSION

Saturation magnetization of obtained nanoparticles was approximately $10 \text{ A}\cdot\text{m}^2/\text{kg}$ for samples *M1*, *M3* and $55 \text{ A}\cdot\text{m}^2/\text{kg}$ for samples *M2*, *Mag50*. Differences of magnetic properties of synthesized nanoparticles one could attribute to different chemical composition of the nanoparticles.

The room-temperature NGR-spectra of the samples *M1*, *M2* and *M3* that were synthesized under ultrasonic treatment include superparamagnetic component (quadrupole doublets) with parameters that are characteristic for high-spin iron (III) ions in octahedral coordination. Change of isomer shifts for resonance doublets of these samples were $0,33 - 0,43 \text{ mm/s}$, and for quadrupole splitting – $0,58 - 0,72 \text{ mm/s}$. The relative areas of superparamagnetic doublets (or iron (III) concentration) for these samples were $\sim 60, 7, \text{ and } 7\%$, correspondingly. If one proceed from the assumption about equality of resonance adsorption coefficients for iron ions of different valences of all phases, than the ratio of resonance components areas would display the ratio of iron concentrations in each phase. Appearance of superparamagnetic component, probably, caused by ultrasonic treatment of nanoparticles and formation of single super-

paramagnetic nanoparticles during the covering procedure. *Figure 1* presents the room-temperature NGR-spectrum of sample *M1*.

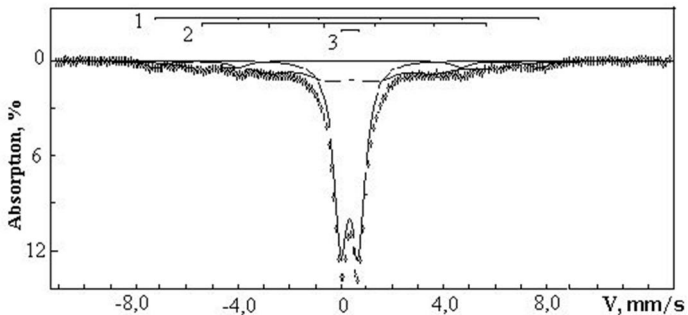


Fig. 1 – Room-temperature NGR-spectrum of sample *M1*. 1 – resonance adsorption sextet of Fe^{+3} in hematite, 2 – resonance adsorption sextet of Fe^{+3} in goethite, 3 – resonance adsorption doublet of Fe^{+3} in superparamagnetic phase

Magnetic components of NGR-spectra of these samples are presented by several Zeeman sextets that are results of resonance absorption in structures of several phases of iron oxides and hydroxides – maghemite, hematite and hydrogoethite. Samples composition is very different. For example, goethite content is varying from several to 80 percent. Presence of oxidized magnetic phases (maghemite, hematite), probably, caused by oxidation of magnetite nanoparticles by atmospheric oxygen due to prolongation of reaction time and increasing of reaction temperature.

NGR-spectrum of sample *Mag50*, consists of six sextets. Two sextets with total area of 41 % are attributed to strongly oxidized magnetite and four sextets – to hydrogoethite. Ratio of concentrations of iron (III) ions in tetrahedral (A) and octahedral (B) positions of magnetite structure to iron (II) and iron (III) ions in octahedral positions based on the areas ratio of corresponding sextets is $\sim 2,14$. This ratio denotes the nonstoichiometry of magnetite composition due to oxidation of iron in octahedral positions. Using this ratio one could determine the number of vacancies in octahedral sublattice and write the magnetite formula. Four sextets of iron (III) in goethite spectrum are related to watering of its structure and formation of four non-equivalent positions of resonance ions.

Thus, the change of concentration ratio $\text{Fe (II)}/\text{Fe (III)}$ greatly affect the obtained phase ratio in magnetic nanoparticles and, correspondingly, saturation magnetization of the sample. For instance, samples *M2* and *Mag50* with saturation magnetization approximately $55 \text{ A}\cdot\text{m}^2/\text{kg}$ contain mainly maghemite and magnetite, correspondingly. Samples *M1* and *M3* with saturation magnetization approximately $10 \text{ A}\cdot\text{m}^2/\text{kg}$ contain mainly hematite and hydrogoethite. Increase

of temperature of covering reaction result in total oxidation of magnetite and formation of maghemite and other iron oxides (samples *M1*, *M2* and *M3*), whereas covering at ambient temperature leads to formation of magnetite (sample *Mag50*). Ultrasonication during the covering procedure brings to formation of superparamagnetic phases (“small” particles), while covering without ultrasonication leads to formation of ferrimagnetic phases (“large” particles).

CONCLUSIONS

Ultrasonic treatment of the magnetic nanoparticles during the covering by silica leads to formation of single superparamagnetic nanoparticles. Covering of magnetic nanoparticles in the absence of ultrasonic treatment leads to aggregation of uncovered nanoparticles and formation of aggregated magnetic nanoparticles.

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