ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2017, Vol. 62, No. 6, pp. 702–710. © Pleiades Publishing, Ltd., 2017.
Original Russian Text ©A.E. Dosovitskii, E.V. Grishechkina, A.L. Mikhlin, D.I. Kirdyankin, V.M. Novotortsev, 2017, published in Zhurnal Neorganicheskoi Khimii, 2017, Vol. 62, No. 6, pp. 715–724.

Effect of the Synthesis Conditions on the Size of Magnetite Nanoparticles Produced by High-Temperature Reductive Hydrolysis

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Received May 5, 2016

Abstract—A study was made into the effect of the conditions (synthesis temperature, water content, iron salt(III) concentration, and nature of precipitant) of the synthesis of magnetite nanoparticles by high-temperature reductive hydrolysis of iron(III) salts in an ethylene glycol medium on their size and morphology. It was shown that is basically possible to carry out the direct synthesis of spherical particles with an average size of 55–170 nm while varying synthesis conditions. The obtained particles were characterized by X-ray powder diffraction analysis, and their magnetic properties were explored. The synthesized particles are ferrimagnets. The magnetic moments, numbers, and sizes of domains in magnetite particles of various sizes were found.

DOI: 10.1134/S0036023617060055

The current development of information technologies (data recording, storage, and retrieval; the need in very-high-speed supercomputers; etc.) requires one to create nanosized magnetic materials for decreasing the size of magnetic memory elements by using smaller particles. Therefore, magnetic nanoparticles along with nanoparticles of another nature are now the subject of active and comprehensive investigation [1].

Of numerous magnetic materials that have found wide technological application, materials based on magnetite (Fe_3O_4) nanoparticles should be noted. Although the first works on the synthesis and study of such materials were published as far back as the 1980s [2], this subject also remains topical today, which is due to the possibility of using Fe_3O_4 nanoparticles in diagnosis and treatment of a variety of diseases, including cancer [3, 4]. Therefore, it is of undoubted interest to develop new methods for synthesizing magnetite nanoparticles and determine the effect of the synthesis conditions on the practically important characteristics (morphology, size) of the produced nanoparticles.

One of the main methods for producing magnetic ultradisperse materials based on magnetite is to perform controllable chemical reactions in various solvent systems. In particular, in one of the first works [2], stable colloidal magnetite was obtained from aqueous solutions containing iron(II) and iron(III) chlorides at various pH. Different modifications of this method are widely used at present [5, 6]. A simple enough method was proposed for producing spherical and cubical magnetite nanoparticles by boiling a $FeCl_3 \cdot 6H_2O$ solution in 2-pyrrolidone in a nitrogen atmosphere [7]; using iron(III) acetylacetonate as a precursor was discussed [8].

One of the methods used currently for synthesizing magnetite nanoparticles is high-temperature reductive hydrolysis of iron(III) salts in a polyol medium [9]. The production of nano- and submicron magnetite particles by high-temperature reductive hydrolysis can be performed under solvothermal conditions without [10, 11] or with preliminary ultrasonication of solutions [12].

However, in the literature, there are no comprehensive data on the effect of the conditions of the synthesis of magnetite nanoparticles by reductive hydrolysis on their size and morphology. Therefore, a further methodological development of this method for producing Fe_3O_4 nanoparticles, which allows one to control the size and size distribution of particles, is important.

In this work, we studied the effect of the conditions of high-temperature reductive hydrolysis of iron(III) compounds in an air atmosphere on the size, size distribution, and magnetic characteristics of the produced particles.

EXPERIMENTAL

Magnetite particles were synthesized from iron(III) chloride hexahydrate $FeCl_3 \cdot 6H_2O$, sodium acetate trihydrate $CH_3COONa \cdot 3H_2O$, sodium propionate C_2H_5COONa, sodium formate HCOONa, ethylene glycol $C_2H_6O_2$, and polyethylene glycol 400 (all analytically pure), and also distilled water. The reagents were used without additional purification.

Sodium salts of monobasic carboxylic acids (acetate, propionate, and formate) were used a precipitant; ethylene glycol, as a dispersion medium and iron(III) reductant; and polyethylene glycol 400, as a stabilizer. The initial water content of the reaction medium was varied from 0.6 to 10 vol %; the initial iron(III) chloride concentration, from 0.02 to 0.1 mol/L; and the synthesis temperature, from 150 to 175°C. In all the experiments, the $Fe^{3+} : CH_3COONa$ molar ratio was 1 : 9 and the Fe^{3+} : polyethylene glycol 400 molar ratio was 10 : 1.

Magnetic nanoparticles were synthesized by premixing the initial reagents with subsequently heating the reaction mixture while intensely stirring and keeping at a given temperature until complete magnetite precipitation.

The size and morphology of the synthesized particles were determined with SU1510 (Hitachi) and JEOL JSM 7100F (JEOL Ltd.) scanning electron microscopes and JEOL JEM-1011 transmission electron microscope. The average size and size distribution of nano- and submicron particles were found by dynamic light scattering with a Zetasizer Nano instrument (Malvern).

The X-ray powder diffraction powder analysis of the obtained samples was made with a D8 ADVANCE diffractometer (Bruker) using CuK_α radiation within the 2θ range 10°–80° at an increment of 0.01°. The unit cell parameter was refined by the Rietveld method using the TOPAS software [13].

The magnetic properties were measured with a PPMS-9 physical property measurement system (Quantum Design) in magnetic fields to 50 kOe. Hysteresis loops were recorded at 300 and 4 K. The samples were placed in polyethylene bags, weighed, compacted (to minimize the displacement of particles within the bags), and sealed.

The product yield was found by direct complexometric titration of iron(III) in the mother liquor (after the synthesis of magnetite particles) [14].

RESULTS AND DISCUSSION

Effect of Synthesis Temperature on Magnetite Particle Size

To determine the effect of the synthesis temperature on the magnetite nanoparticle size, the product obtained at a temperature of 150–175°C and an initial water content of 3.0 vol % was characterized by scanning electron microscopy. For analysis, a sample was taken from the reaction medium and washed several times with distilled water to remove synthesis by-products and reagents.

According to the scanning electron microscopy data, the product obtained at 150°C was a bulky porous structure (Fig. 1a); also noteworthy is that the sample had no magnetic properties. Increasing synthesis temperature to 160°C gave rise to agglomerates several micrometers in size, which had magnetic properties (Fig. 1b). At a synthesis temperature of 170°C, spherical particles 50–70 nm in diameter began to form in the system (Fig. 1c). The product synthesized at 175°C comprised individual spherical particles ~200 nm (Fig. 1d).

The average size and size distribution of magnetite particles produced at 175°C were determined by dynamic light scattering (Fig. 2a). To confirm the obtained data, this sample was also analyzed by high-resolution scanning electron microscopy (Fig. 2b).

The results of determining the particle size by dynamic light scattering and scanning electron microscopy differ. According to the dynamic light scattering data, the particle diameter is 173 ± 30 nm (Fig. 2a), and according to the scanning electron microscopy data, it is 120 ± 20 nm (Fig. 2b). The differences between the obtained data are explained by the fact that the dynamic light scattering method can determine the hydrodynamic radius of particles (which is almost always overestimated because of the presence of a solvation shell).

The transmission electron microscopy showed that the synthesized particles are agglomerates of smaller particles (Fig. 2c). It can be assumed that the final stage of the formation of nanoparticles consists of two successive steps, at the first of which "primary" nanoparticles 3–15 nm are produced, and at the second they aggregate to give spherical structures. Spherical magnetite structures of such a morphology form at certain temperatures, the range of which is limited by the boiling point of aqueous ethylene glycol solutions.

Effect of Water Concentration on Magnetite Particle Size

For the system under investigation, the dependence of the particle size on the initial water concentration was determined. The initial iron(III) solt concentration was 0.05 mol/L, and the $Fe^{3+} : CH_3COONa$ molar ratio was 1 : 9. Table 1 presents the obtained data.

With increasing initial water content from 0.6 to 10.0 vol %, the diameter d_p of the synthesized particles decreases (Fig. 3). According to the scanning electron microscopy data, at water concentration of 0.6–1.0 vol %, particles of an average size of <100 nm and agglomerates 2–7 μm in size are produced in the system. At water concentrations of 2 vol % and more, individual spherical particles form. Increasing initial water con-

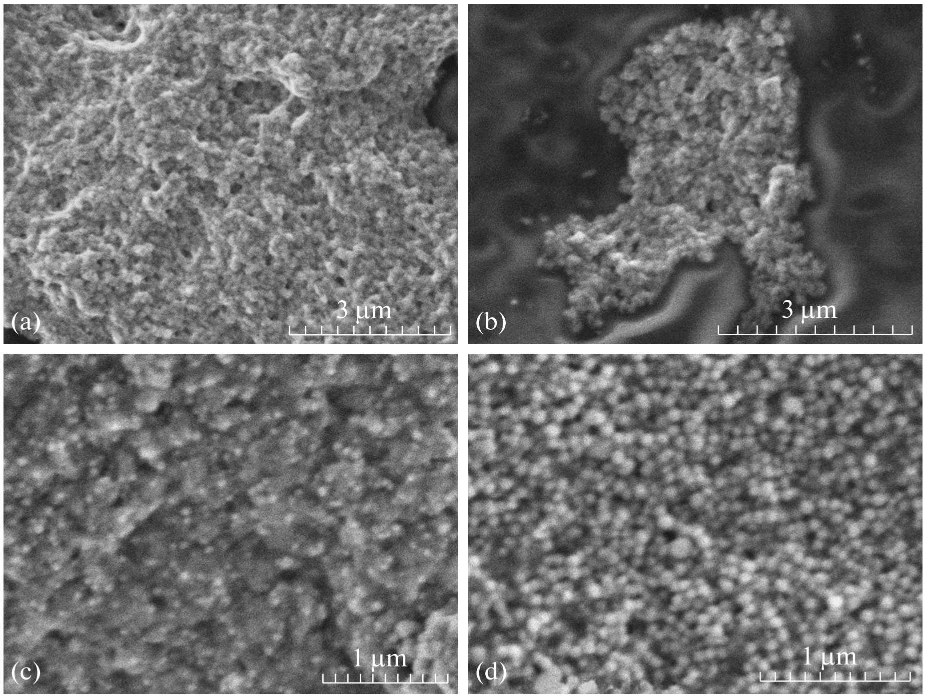

Fig. 1. Micrographs of magnetite particles produced at synthesis temperatures of (a) 150, (b) 160, (c) 170, and (d) 175°C.

tent from 2 to 4 vol % leads to an increase in the average magnetite particle size. With a further increase in the water content from 8.0 vol %, the average particle size decreases to ~55 nm and the dispersity of the particles also decreases. At a water concentration of 10.0 vol %, magnetite does not form.

It was shown above that the synthesis of magnetite particles by high-temperature reductive hydrolysis of iron(III) compounds in air occurs at a temperature close to the boiling point of the reaction mixture. With increasing water content of the ethylene glycol–water mixture, its boiling point decreases, which also enables to decrease the temperature of the synthesis of magnetite particles. For example, with increasing initial water content from 0.6 to 10 vol %, the synthesis temperature decreases from 190 to 145°C (Table 1). The change in the particle size with varying water content is likely to be caused by performing the synthesis at markedly different temperatures.

It was also found (Table 1) that increasing initial water content of the reaction mixture hardly influences the product yield, which in all the cases was ~100%.

Thus, the particle size can be affected by two parameters: synthesis temperature and water concentration. The presence of water in the reaction medium is a must because water participates in the hydrolysis of intermediate compounds necessary for the synthesis of magnetite particles.

Based on the results obtained, it can be concluded that an elevated (in comparison with the stoichiometric value for ensuring hydrolytic processes) initial water content of the reaction mixture makes it possible to perform the synthesis at lower temperatures and

Table 1. Comparative characterization of the conditions of the synthesis of Fe_3O_4 particles, their size and morphology, and the product yield at an initial iron(III) salt concentration of 0.05 mol/L

Parameter	Initial water content, vol %								
	0.6	1.0	2.0	3.0	4.0	5.0	6.0	8.0	10.0
$T_{\text{synthesis}}$, °C	190	188	185	175	170	165	160	150	145
d_p, nm	50–50000	50–5000	40–60	100–140	100–180	100–180	80–110	55–60	–
Morphology	Spheres	Agglomerates of indeterminate shape	Spheres	Spheres	Spheres	Spheres	Spheres	Spheres	–
Yield, %	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9	–

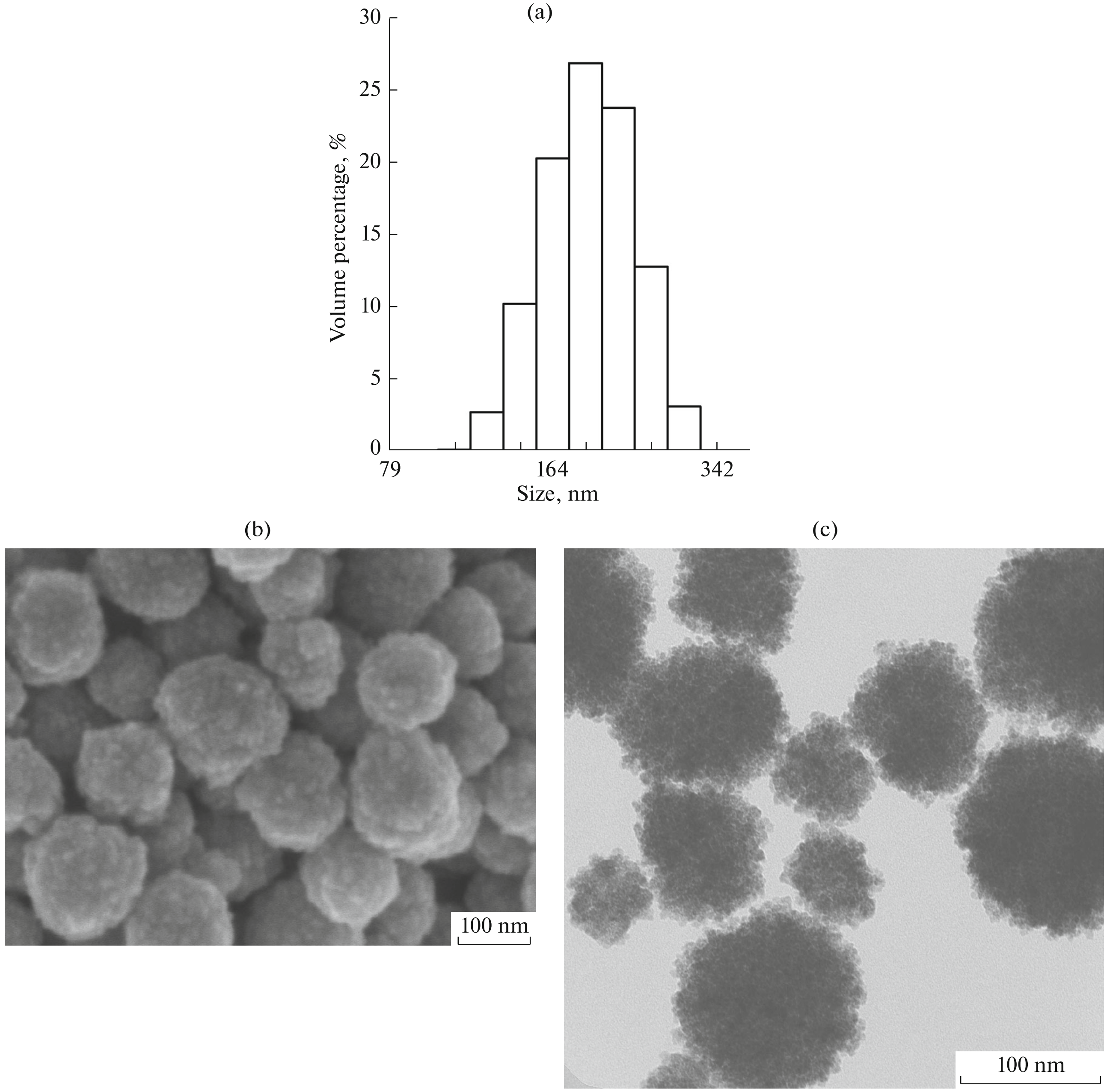

Fig. 2. (a) Size distribution histogram of magnetite particles and their micrographs taken by (b) scanning and (c) transmission electron microscopy.

vary the size of the produced Fe_3O_4 particles over a wide range.

Effect of Nature of Precipitant on Magnetite Particle Size

To determine the effect of the nature of precipitant on the magnetite particle size, sodium salts of the neighboring homologues in a series of monobasic carboxylic acids (formate, acetate, and propionate) were chosen. The synthesis was conducted under identical conditions: the Fe^{3+} concentration was 0.05 mol/L, the synthesis temperature was 175°C, and the initial water content was 3.0 vol %.

The obtained data showed that the syntheses using sodium formate, acetate, and propionate give spherical particles of diameters of 100–180, 100–140, and 60–90 nm, respectively (Fig. 4).

The differences in size between the produced particles are likely to be caused by the differences between the rates of the hydrolysis of intermediate iron(III) compounds and the rate of magnetite formation. When dissolving in the reaction medium, precipitants

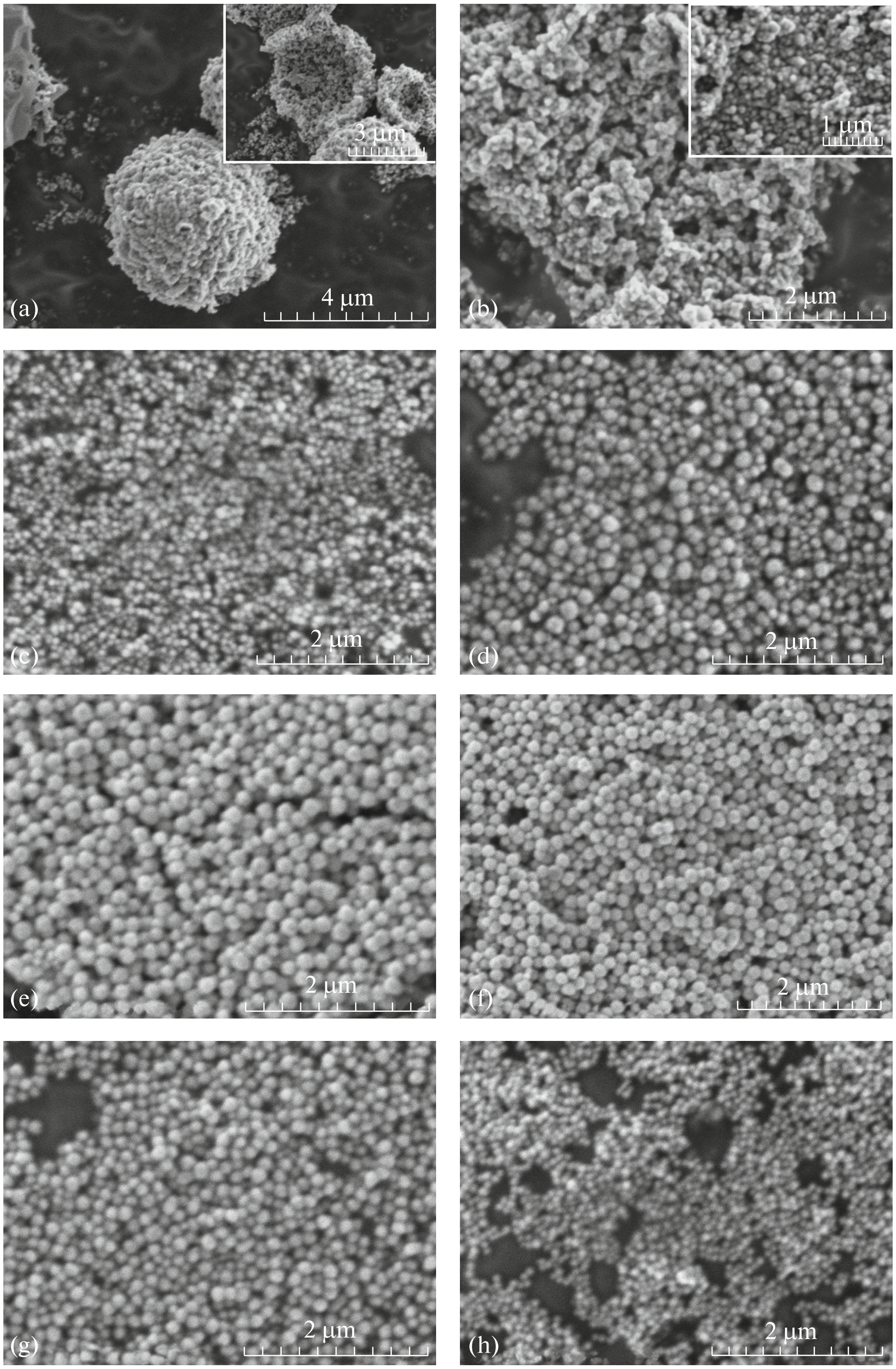

Fig. 3. Micrographs of magnetite particles produced using sodium acetate at various water contents (vol %): (a) 0.6, (b) 1.0, (c) 2.0, (d) 3.0, (e) 4.0, (f) 5.0, (g) 6.0, and (h) 8.0.

dissociate, and carboxylate anions are adsorbed on the formed systems, participating in their stabilization. However, because of the difference in structure between carboxylate anions produced by the dissociation of participants, their adsorption properties may differ, which also influences the magnetite particle size.

Effect of Precipitant Concentration

The particle size can be affected by the precipitant concentration because increasing iron(III) salt concentration increases supersaturation. The initial iron(III) salt concentration was varied from 0.02 to 0.1 mol/L. The precipitant was sodium acetate, the

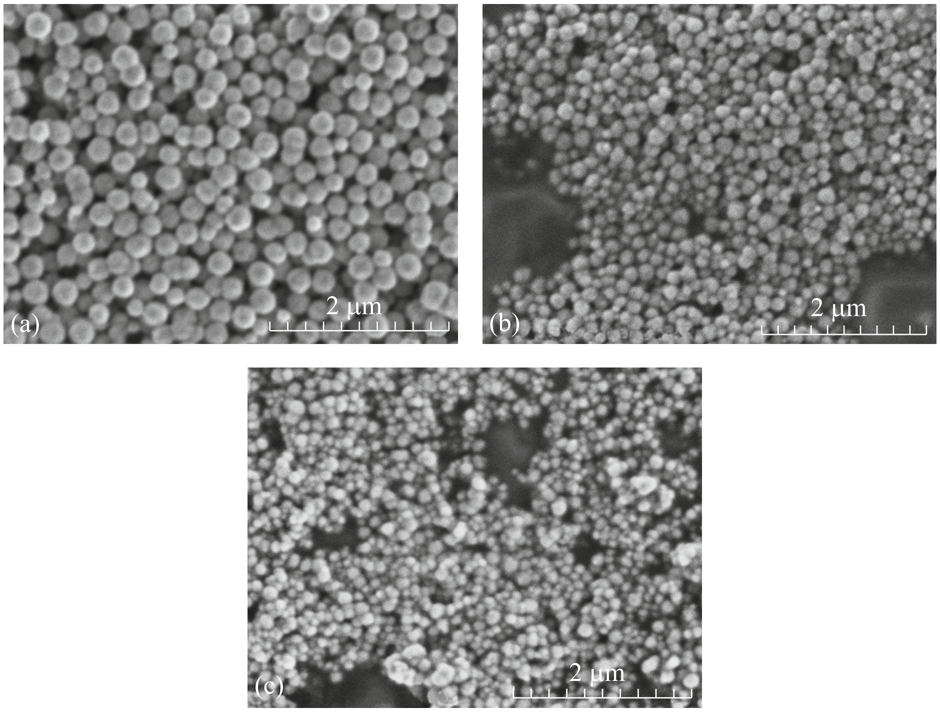

Fig. 4. Micrographs of magnetite particles produced using various precipitants: (a) sodium formate, (b) sodium acetate, and (c) sodium propionate.

Fe^{3+} : CH_3COONa molar ratio was 1 : 9, the synthesis temperature was 175°C, and the initial water content was 3.0 vol %.

Scanning electron microscopy of the obtained magnetite samples demonstrated that, with increasing initial Fe^{3+} concentration from 0.02 to 0.1 mol/L, the average magnetite particle size increases from 80 to 190 nm (Table 2). Moreover, the scanning electron microscopy showed that, throughout the concentration range, spherical particles form.

X-ray Powder Diffraction Analysis of Magnetite Particles

To determine the phase composition, X-ray powder diffraction analysis of the obtained Fe_3O_4 nanoparticles was made, the average sizes of which according to the scanning electron microscopy data are 80 and 120 nm.

Table 2. Dependence of the average magnetite particle size on the initial Fe(III) concentration

Fe(III) concentration, mol/L	Particle size, nm
0.02	80 ± 10
0.05	120 ± 20
0.075	100 ± 40
0.10	170 ± 30

It is known that the structures of γ-Fe_2O_3 (maghemite) and Fe_3O_4 (magnetite) are quite similar, and the lattice periods of the maghemite and magnetite (of stoichiometric composition) differ insignificantly: 0.8397 nm (magnetite) and 0.8347 nm (maghemite). This complicates their unambiguous identification by X-ray powder diffraction analysis, especially in the nanosized state [15–17]. An X-ray diffraction method was proposed [18], which includes an analysis of high-angle peaks (511) and (440). Earlier [19], by ^{57}Fe Mössbauer spectroscopy of magnetite Fe_3O_4 nanoparticles synthesized by high-temperature reductive hydrolysis, we showed that the main phase is $Fe_3O_{4+\delta}$.

Thus, based on our previous results [19] according to the published procedure [18], we can assume that the synthesis produces iron oxides with the spinel structure (space group $Fd\bar{3}m$) (Fig. 5). The lattice period *a* and the average size of crystallites were refined by the Rietveld method (Table 3). The average size of crystallites correlates with the scanning electron microscopy data on the size of particles constituting agglomerates of spherical structures.

Magnetic Properties of Magnetite Particles

The magnetic properties were studied on magnetite particles with average sizes of 80 and 120 nm (according to the scanning electron microscopy data).

For particles with an average size of 80 nm, the saturation magnetization is 11.4 G cm^3 g^{-1} at 300 K and

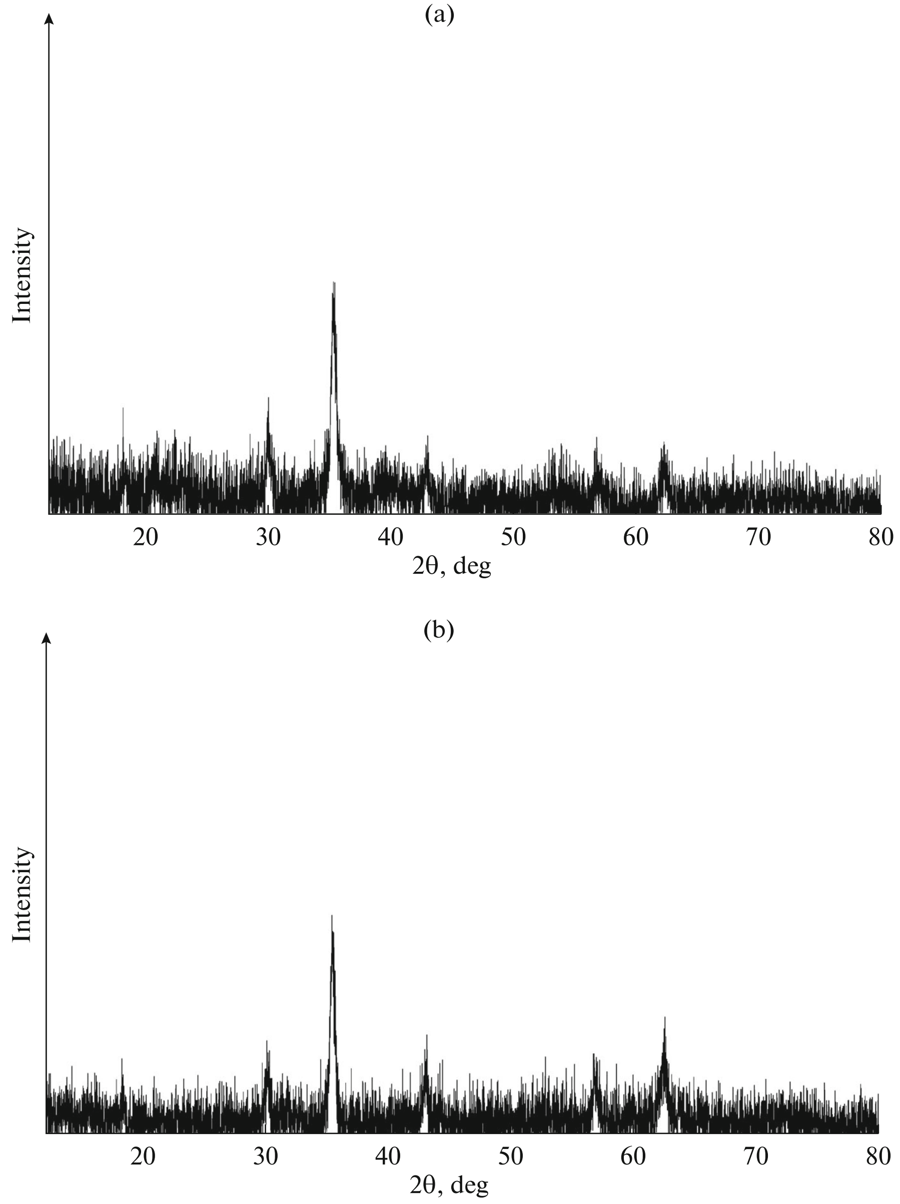

Fig. 5. X-ray powder diffraction patterns of magnetite particles with average sizes of (a) 80 and (b) 120 nm.

14.4 G cm^3 g^{-1} at 4 K, the coercivity is 9 Oe at 300 K and 260 Oe at 4 K, and the remanence is 0.6 G cm^3 g^{-1} at 300 K and 4.6 G cm^3 g^{-1} at 4 K (Fig. 6).

For particles with an average size of 120 nm, the saturation magnetization is 38.6 G cm^3 g^{-1} at 300 K and 47 G cm^3 g^{-1} at 4 K, the coercivity is 12 Oe at 300 K and 275 Oe at 4 K, and the remanence is 1.2 G cm^3 g^{-1} at 300 K and 16.8 G cm^3 g^{-1} at 4 K.

Bulk magnetite is a ferrimagnet with a saturation magnetization of 80–100 G cm^3 g^{-1} at 300 K [20].

The field dependences of the magnetization were described by the Langevin equation $\sigma(H) = C[\coth bH - (1/bH)]$ [9], where the parameters C and b are related to the saturation magnetization and magnetic domains of particles: $C = N\mu$ and $b = \mu/k_BT$. Here, N is the number of magnetic domains in 1 g of sample; μ is the magnetic moment of domains; k_B is the Boltzmann constant (1.38×10^{-16} Oe K^{-1}); and T is temperature.

Table 3. Results of X-ray powder diffraction analysis of magnetite particles (SEM is scanning electron microscopy)

Average particle size (SEM), nm	Lattice period, nm	Average crystallite size, nm
120	0.8417	13.6
80	0.8432	11.1

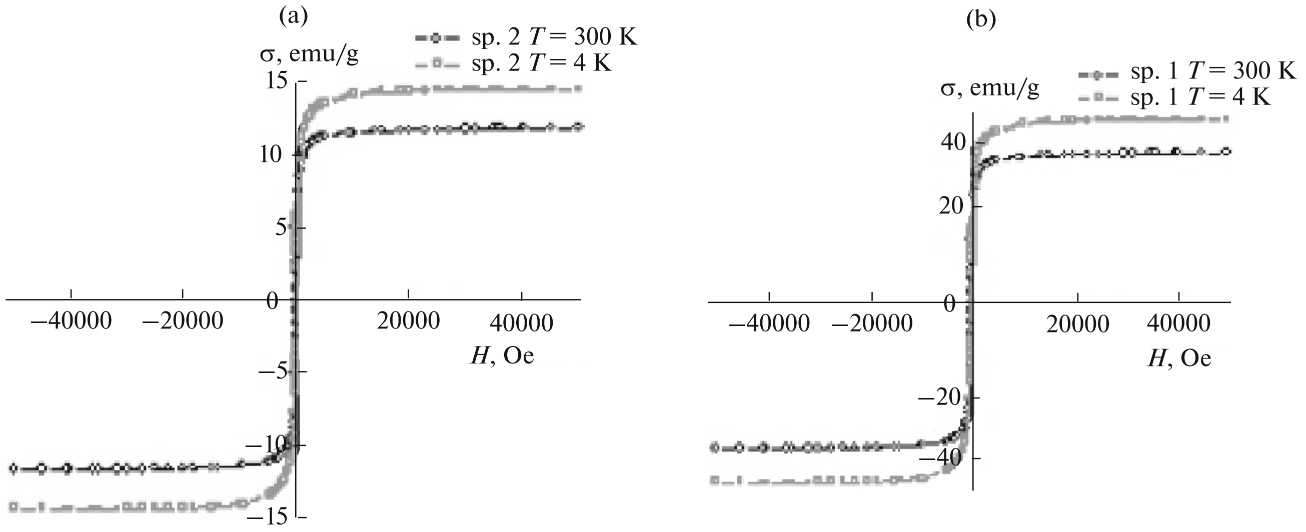

Fig. 6. Field dependence of the magnetization of magnetite particles with average sizes of (a) 80 and (b) 120 nm at 300 and 4 K.

Using these formulas, the magnetic moment of domains and their number and size d at 4 and 300 K. The size of domains was calculated using the unit cell parameter values obtained by processing the X-ray powder diffraction analysis data. Magnetite is known to have the inverse spinel structure with 32 oxygen atoms (8 formula units) per Fe_3O_4 unit cell; they form an fcc lattice, in which Fe^{3+} and Fe^{2+} ions occupy octahedral and tetrahedral positions, respectively. The total moment μ_{uc} of the unit cell is $48\mu_B$ (4.45×10^{-19} erg/G), where μ_B is the Bohr magneton (9.27×10^{-21} erg/G).

Because $\mu_{uc}/V_{uc} = \mu/V_d$, where V_{uc} is the unit cell volume, m^3, and V_d is the magnetic domain volume, m^3, the domain size is

$$d = (a^3\mu/48\mu_B)^{1/3}.$$

Table 4 presents the data obtained for particles of various sizes at 4 and 300 K. Table 4 shows that, with decreasing temperature, the size of domains decreases by a factor of ~4.5 and their magnetic moment decreases by two orders of magnitude. At 300 K, to a decrease in the magnetite particle size from 120 to 80 nm, an increase in the domain size from 71 to ~80 nm corresponds. The magnetic moment of domains also increases. The opposite situation is observed at 4 K. With increasing temperature, the domain wall of clusters moves much faster, which leads to the growth of the cluster; the increase in the cluster moment and size is related to it. Because the domain size at 4 K is much smaller than the particle size, the particles are multidomain; then, with increasing temperature (or field), the domain should occupy the entire particle.

At 300 K, the magnetite particles with an average size of 80 nm can be considered single-domain because their average size virtually coincides with the domain size (~80 nm). However, in the magnetite particles with an average size of 120 nm, the domain does not occupy the entire particle because of the shortage of energy (instability of large domains); hence, this is the most energy-preferable state, in which the particle is divided by half by domains with an average size of ~70 nm. The merger of two domains ~70 nm in size into one has a significant energy barrier and is likely to occur at much higher temperature. At lower temperatures, the most preferable domain size is virtually independent of the Fe_3O_4 particle size and is ~14 nm, whereas the total domain moment is ~2×10^{-18} erg/G.

Based on the results of analyzing the obtained data, we can conclude that, by varying the synthesis conditions (synthesis temperature, water content, iron(III)

Table 4. Calculated values of the magnetic moment μ and the number N and size d of domains of magnetite particles of various sizes

Particle size, nm	T, K	μ, erg/G	N, units/g	d, nm
120	300	2.77×10^{-16}	1.39×10^{17}	71.9
	4	2.45×10^{-18}	1.92×10^{19}	14.9
80	300	3.79×10^{-16}	3.02×10^{16}	79.9
	4	1.91×10^{-18}	7.57×10^{18}	13.7

salt concentration, and nature of precipitant), one can produce spherical particles with average sizes of 55 to 170 nm, which are agglomerates of particles 3–15 nm in size. The X-ray powder diffraction analysis showed that the synthesized product has the spinel structure and belongs to the space symmetry group $Fd\overline{3}m$. The magnetic studies of the obtained particles demonstrated that they are ferrimagnets with a saturation magnetization of 11.4 G cm^3 g^{-1} (300 K) for particles with an average size of 80 nm and 38.6 G cm^3 g^{-1} (300 K) for particles with an average size of 120 nm. With decreasing temperature to 4 K, the saturation magnetization increases to 14.4 and 47 G cm^3 g^{-1}, respectively. This also leads to a decrease in the magnetic moment of domains to ~2×10^{-18} erg/G and in their size to ~14–15 nm.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Education and Science of the Russian Federation (agreement no. 14.576.21.0002 of June 17, 2014, UI RFMEFI57614X0002).

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Translated by V. Glyanchenko