Synthesis of Fine-Grained Calcium Hexaferrite and Investigation of Its Structural and Magnetic Parameters

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Abstract—The results of investigations aimed at creating a system of fine-grained crystals of calcium hexaferrite doped with lanthanum (barium) are presented. An integrated technological approach that involves two cycles is implemented. At the first stage, i.e., the stage of preparing the charge mixture, a high-efficiency cryochemical technology that allows one to obtain a chemically homogeneous (at the atomic level) ferrite charge mixture was used. At the second stage, namely the stage of ferritization, 1.2–4.8 wt % of a low-melting flux was added to an oxide charge mixture of ferrite that made it possible to reduce the temperature of complete ferritization and, thus, to create the conditions for formation of nano- and microcrystals of a specified composition. The specimens of the synthesized magnetic powder demonstrated magnetic properties at the level of the best microcrystalline systems of barium hexaferrite.

INTRODUCTION

Micro- and nanocrystalline hexaferrite structures of type M are interesting objects for investigating specific properties of small particles and turn out to be very promising for perfecting high-density magnetic recording, magnetic fluids, medical means of supply, and the retention of medicamental materials in an organism, as well as for hyperthermia of malignant cells.The selection of calcium ferrites for medical application is justified due to its better biological compatibility with other base compositions than alkaline-earth hexaferrites.

A typical chemical composition for M-type ferrites is described by the formula $MeFe_{12}O_{19}$ ($MeO \cdot 6Fe_2O_3$)), where M can be Ba, Sr, or Pb. According to a phase diagram of the $CaO–Fe_2O_3$ system, calcium hexaferrite does not possess the structure of magnetoplumbite, despite its chemical similarity to strontium and barium; it is related to a smaller ion radius of Ca^{2+} (0.106 nm) as compared to Ba^{2+} (0.143 nm), Sr^{2+} (0.127 nm), and Pb^{2+} (0.132 nm). Nevertheless, it was revealed that the addition of lanthanum oxide to the initial system can yield the formation of an M phase [1–3]. The authors of [4] proposed a possible mechanism for its formation where $CaO \cdot 2Fe_2O_3$ with a hexagonal structure plays the role of a precursor. Though lanthanum can serve as a ligand for the formation of a calcium hexaferrite M phase, other rare-earth elements do not possess these properties. It is explained by an ion radius decrease in the lanthanoid row [5]. A magnetoplumbite structure is observed in the systems of calcium hexaferrite doped with barium [6–8].

To obtain ferrite materials, a ceramic method [9–12], mechanical activation [13–14], a method of coprecipitation [15–16], sol–gel methods and their variations [17–20], pyrolysis of aerosols [21, 22], a cryochemical technology and its modifications [23–25], a method based on fast expansion of supercritical solutions [26], etc. are extensively used.

This paper presents the results of investigations aimed at creating a system of fine-grained crystals of calcium hexaferrite. An integrated technological approach to obtaining fine-grained calcium hexaferrite, which has not yet been synthesized, that includes two technological cycles is proposed. At the first stage, i.e., the preparation of a charge mixture, high-efficiency cryochemical technology was used that made it possible to obtain a chemically homogeneous (at the atomic level) ferrite precursor.

TECHNOLOGY OF SYNTHESIS FINE-GRAINED PRECURSOR

The use of fine-grained and highly homogeneous precursors makes it possible to obtain ferrites that are hard to synthesize using other methods and to drastically increase the process of phase formation. The idea of the technology can be reduced to obtaining a fine-grained and highly homogeneous salt precursor via the fast freezing of a finely atomized salt solution and the subsequent sublimation removal of water.

Previously, the authors performed experiments [27–28] on producing powdered barium hexaferrite that demonstrated the advantages of the cryochemical technology of nanodispersed precursor preparation. The experience thus acquired was used in the present study to synthesize new materials, i.e., calcium hexaferrite doped with lanthanum oxide and calcium hexaferrite doped with barium. Acetates of calcium, lanthanum, and ferric iron, as well as barium nitrate were used as source salts for synthesis.

The key technological stages of the cryochemical method [1] of obtaining nanopowders of salts as a target product are as follows:

– preparation of the solution;

– dispersion of the solution with simultaneous freezing of drops into solid grains;

– removal of the solvent from the grains by sublimation (cryoextraction, cryoprecipitation).

The following technological operations are additionally performed for ferrite compositions:

– dehydration and thermal decomposition of precursor compounds;

– formation and sintering of ferrite compositions.

An analysis of the literary data shows that it is expedient to use the salts of acetic acid as salts of the initial components. The use of nitrates is hindered by the low melting temperatures of the solutions, whereas chlorides are very volatile substances. Acetates of iron (III), calcium, and rare-earth elements (REE) are well soluble in water and are characterized by fairly high melting temperatures of frozen solutions.

In the present study, a solution containing a mixture of initial salt solutions was atomized into an inert refrigerant, i.e., liquid nitrogen. The main method of removing a solvent from cryograins is sublimation drying. Sublimation was performed at a lower pressure than that corresponding to the triple point of the solvent on the temperature–pressure diagram. This makes it possible to minimize the agglomeration of product particles formed at the freezing stage due to the elimination of liquid-phase formation in the material. In practice, the quality of sublimation drying is evaluated by the absence of submelting traces in a dried product. The drying conditions are selected using plots of low-temperature differential thermal analysis (DTA) (Fig. 1).

The obtained dry mixture of salts was subjected to a derivatographical analysis (Fig. 2) that makes it possible to determine the stages of phase formation in the process of ferrite synthesis as functions of temperature. A derivatogram was used to estimate the temperature of annealing for the obtained mixture of salts. Furthermore, it was important to obtain a ferrite at the lowest possible temperature that, first, is energetically advantageous and, second, makes it possible not to permit secondary recrystallization of the product, which yields an increase in particle size. The process of annealing ensured the necessary conditions of convection for the removal of gaseous products of initial salt decomposition.

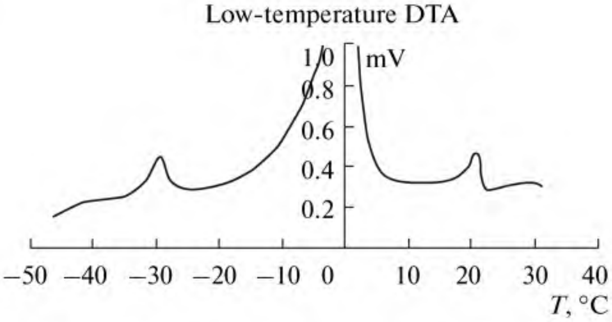

Fig. 1. The result of low-temperature DTA for the mixture of Ca, Fe, and La acetates.

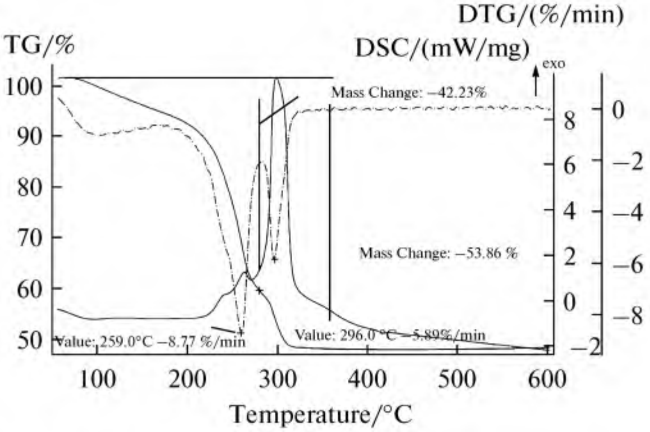

Fig. 2. A derivatogram for the mixture of Ca, Fe, and La acetates.

In the present study, sublimation drying was accomplished using the Advantage ES-53 sublimator (VirTis, United States) in a stainless-steel tray. The automatic drying mode followed the following program:

Platform temperature, °C	Time, min
–30	120
–30 ⟶ –15	120
–15	300
–15 ⟶ –10	60
–10	240
–10 ⟶ 0	120
0	300
0 ⟶ 30	120
30	360

In the process of drying, the average temperature on the condenser of approximately –50°C and a pressure of 2.66–13.3 Pa were sustained. Mass variations (TG)

The ratio of the main substances in initial compositions

No. of composition	Ratio of molar fractions of initial substances			
	Ña	Fe	La	Ba
1	0.978	11.603	0.419	–
2	1	12	–	–
3	0.5	12	–	0.5

and calorimetric effects (DSC) during specimen heating were accomplished using an STA 449 C Jupiter synchronous thermoanalyzer (NETZSCH, Germany). The following parameters were used for the TG/DSC analysis:

– mass loss of 55–60%,
– heating rate of 2°/min,
– heating from room temperature to 600–700°C.

INVESTIGATION OF PROCESSES OF SYNTHESIS OF CALCIUM HEXAFERRITE DOPED WITH LANTHANUM

The initial compositions of the studied specimens are listed in Table 1.

The products of cryochemical synthesis were decomposed in air in a SNOL-10/11-I1 convective-type muffle electrical furnace (TOO Tekhnoterm, Russia) .

Some of the products of cryogenic synthesis were decomposed at temperatures of 400–900°C in a nickel tray placed into a furnace heated to the required temperature for a specified period of time (10 min). Furthermore, a mixture of salts was distributed over the tray in a 3–5-mm-thick layer. Alundum melting-pots filled with a 4–7-mm-thick powder layer were used for annealing at a temperature of 1000–1100°C.

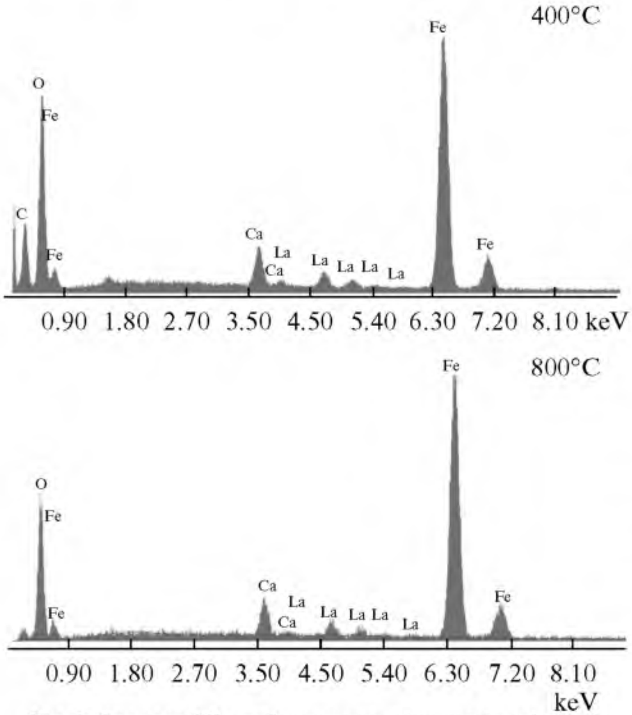

Fig. 3. Spectra of X-ray fluorescence elemental analysis of the specimens annealed at different temperatures.

After being taken out of the furnace, the melting pots and tray were cooled at room temperature. A TG/DSC analysis made it possible to analyze the process of thermolysis of the products of cryogenic synthesis.

During heating to a temperature of 100–110°C, La acetate begins to decompose according to the following scheme:

$$\mathrm{La(CH_3COO)_3 \cdot (H_2O)_x \rightarrow La(CH_3COO)_3}$$
$$\mathrm{\rightarrow La_2O_2CO_3 \rightarrow La_2O_3.}$$

Anhydrous lanthanum acetate is stable up to 250°C and decomposes to oxycarbonate at 440°C [30].

The decomposition of Ca acetate at 160°C can be represented as follows:

$$\mathrm{Ca(CH_3COO)_2 \xrightarrow{160^\circ C} Ca_2C_2O_4}$$
$$\mathrm{\xrightarrow{200^\circ C} CaCO_3 \xrightarrow{850^\circ C} CaO.}$$

The main portion of the exothermal effect and mass loss falls at the decomposition of formate-acetate of ion (III). A peak on the derivatogram (Fig. 2) at 300°C corresponds to the appearance of Fe_2O_3 [31].

At the first stage of investigations, thermolysis for the mixture of Fe, Ca, and La acetate was performed at different temperatures in the range of 400–900°C with a 100°C interval. Diffractograms and electron microphotographs were obtained for all thermolysis specimens, and an elemental microanalysis was made (Figs. 3, 4). The results of the microanalysis confirm the good homogeneity of the distribution of components in the specimen.

The selection of temperatures below the melting point of calcium carbonate (825°C) is explained by the ability of $Ca(CH_3COO)_2$ to decompose to CaO without an intermediate $CaCO_3$ phase. This effect is possible when a product of sublimation drying is immediately placed into a furnace heated to the required temperature. In fact, an X-ray fluorescent elemental analysis shows a gradual decrease in the concentration of oxygen and carbon in specimens as early as at an annealing temperature of 600°C, which indicates the negligible contribution of the $CaCO_3$ phase.

Prior to thermal processing, the specimens of a charge mixture are roentgenoamorphous; however, after thermolysis, weak diffraction peaks appear on the diffractograms at just 400°C (Fig. 8). The main substance in the specimens at temperatures lower than 700°C is Fe_3O_4. Compounds of Fe(II) are formed due to the reduction of Fe(III) by the products of thermal decomposition of acetic acid. The oxide of Fe(III) appears at 600°C and becomes a dominant phase at 800–900°C (Fig. 9). The gradual heating of specimen no. 1 up to 1290°C for 4 h yielded formation of pure cal-

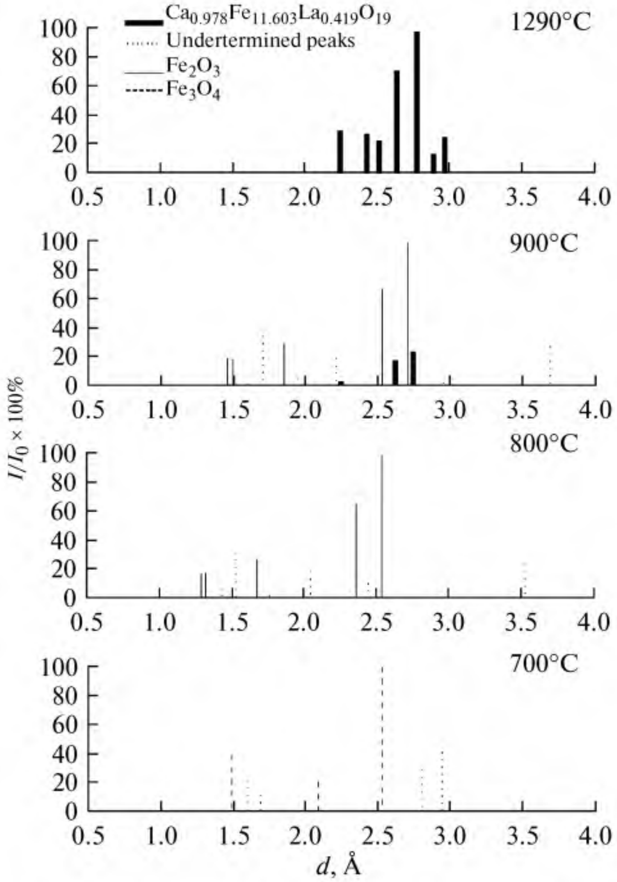

Fig. 4. Bar-diagrams of the specimens of Ca, La, and Fe acetate thermolysis during slow heating for 4 hours at 1290°C (a) and for 10 minutes at the temperatures of 900°C (b), 800°C (c), and 700°C (d).

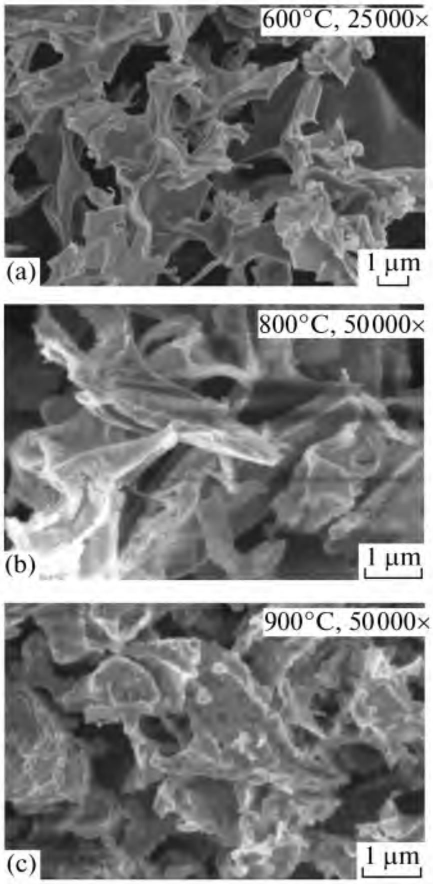

Fig. 5. Electronic microscopic images of the specimens annealed at different temperatures.

cium hexaferrite doped with lanthanum (Fig. 9a). However, at this temperature, a fine-grained ferrite precursor bakes into a nearly solid mass. It can be seen from a comparison of diffractograms (a) and (b) in Fig. 9 that a small amount of the M phase appears as early as at 900°C. For specimen no. 2, a magnetic hexoferrite phase did not appear at any annealing temperature, which confirms the known fact concerning its instability related to a small radius of a calcium ion.

The results of electron microscopy for the specimens of thermolysis of the charge mixture with composition no. 1 (Table 1) are shown in Fig. 5. It can be seen that, after thermolysis, the specimens are agglomerates whose separate cross sections are in the nanosize range.

The results of the X-ray phase analysis are also confirmed by the magnetic action on the specimens. The powder obtained at 800°C with a dominant α-Fe_2O_3 phase (not possessing magnetic properties) demonstrated almost no magnetic susceptibility. The other specimens showed a better magnetic susceptibility that confirms the predominance of Fe_3O_4 during annealing up to 700°C the and formation of a hexagonal phase at 900°C.

The specimen annealed at a temperature of 1290°C nearly bakes into a monolith. To obtain a single-phase material in the form of fine-grained doped calcium hexaferrite, it was necessary to decelerate the process of the recrystallization of the powder particle. This was accomplished by decreasing the temperature of ferritization of the initial oxide mixture. To this end, an addition of a ferrite precursor doped with lanthanum in the form of a low-melting flux was introduced to the oxide mixture. Experiments with the thus-modified material showed that an addition of 1.2–4.5 wt % of barium chloride dehydrate $BaCl_2 \cdot 2H_2O$ as a flux makes it possible to decrease the temperature of complete ferritization by 200–300° and, thus, to create the conditions for the formation of microcrystals with a specified composition in the form of particles with transverse dimensions on the order of 1 μm (Fig. 6). The particles are plate-shaped as hexahedrons (or have a close shape), i.e., their shape is characteristic of hexaferrite. Particle distribution over the diameter d is within the micrometer range, i.e., the particle size corresponds to a single-domain state ($d \leq 1.5$ μm), and the aspect ratio is $d/h = 3$–5 (where h is the particle thickness).

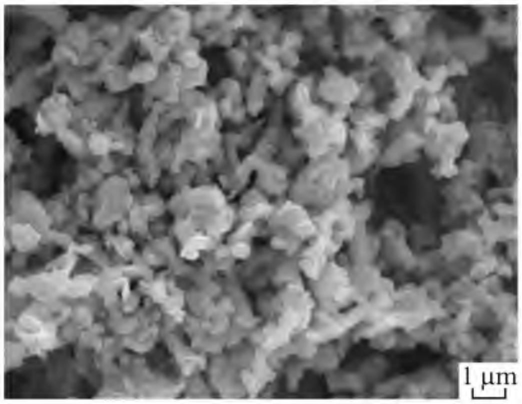

Fig. 6. An electronic microscopic image of a specimen doped with lanthanum.

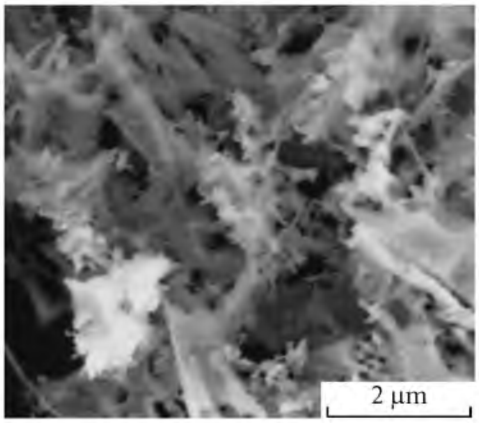

Fig. 7. Hexaferrite $Ca_{05}Ba_{05}Fe_{12}O_{19}$ annealed for 1 hour at the temperature of 900°C.

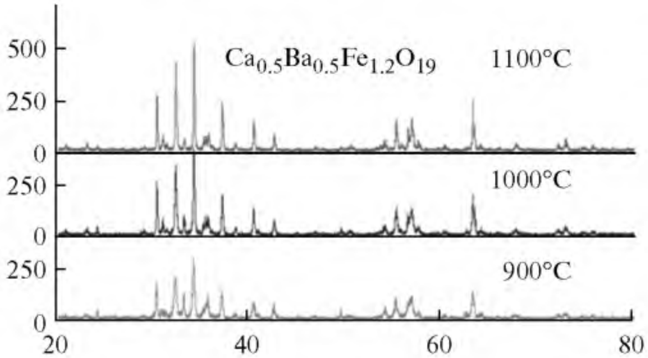

Fig. 8. X-ray diffractograms of hexaferrite specimens doped with barium obtained at different annealing temperatures.

INVESTIGATION OF SYNTHESIS OF CALCIUM HEXAFERRITE DOPED WITH BARIUM

The revealed effect of the flux on the ferritization temperature served as a departing point for creating a new powdered specimen of an M-type Ca ferrite with barium serving as a doping component. Barium nitrate was used as a barium salt in the experiment. The first data of the X-ray phase analysis of specimen no. 3 showed an increase in the M-phase concentration compared to the specimen doped with La at the same temperatures. The results of the electron microscopy of a specimen made of the new material showed a substantial effect of crystallization from a gas phase on agglomerate formation. The formed particles were tree-shaped (Fig. 7).

The temperature of the beginning of M-phase formation was determined to be 650°C for specimens of calcium hexaferrite doped with barium.

Figure 8 gives the results of an X-ray structural analysis of the specimens obtained at different annealing temperatures. It is apparent from the figure that diffraction spectra typical for a magnetic hexaferrite phase were observed in all three specimens. This indicates the single-phase nature of the material of specimens obtained at each of the aforementioned annealing temperatures in the range of 900–1100°C. The form of the Mossbauer spectra for nanodispersed calcium hexaferrite doped with barium obtained for the specimens annealed at different temperatures (see Fig. 9) also indicates the single-phase nature of the specimens, as well as that their magnetic structure belongs to a hexagonal class of M-type ferrites.

INVESTIGATION OF MAGNETIC PROPERTIES OF SYNTHESIZED MATERIAL

Using the synthesized specimens of hexaferrite doped with barium, the following main magnetic parameters were studied at 300°C: the specific saturation magnetization σ_S and the coercive force H_c. To this end, the principle magnetization curve $\sigma(H)$ and the branch of the hysteresis loop were measured in predemagnetized specimens (Fig. 10).

The factor of the powder particle package in the specimen was $p \sim 0.4$. Electrolytic Ni ($\sigma_0 = 53.6\ \mathrm{G\ cm^3\ g^{-1}}$) was used as a reference specimen. The constant of the used pendulum magnetometer was $C' = \frac{\sigma_o m_o}{(i_k/H)_o} = 110 \times 10^{-3} \frac{\mathrm{G\ cm^3\ к}}{\mathrm{mA}}$. The calculation formula was $\sigma = C' \frac{i_k/H}{m}$.

Taking into account that, in addition to the constant of magnetocrystalline anisotropy, the value of the coercive force shows a degree of particle imperfection (structural defects and deformational and twin defects of the package) that allows one to reach the next conclusion. The obtained value of the coercive force of the studied specimen $H_c = 4500$ E is comparable to that of a densely-packed microcrystalline ($d = 0.1$–0.9 μm) powdered specimen ($p \sim 0.4$) of $BaFe_{12}O_{19}$ ($H_c = 4000$–4450 E at 300°C).

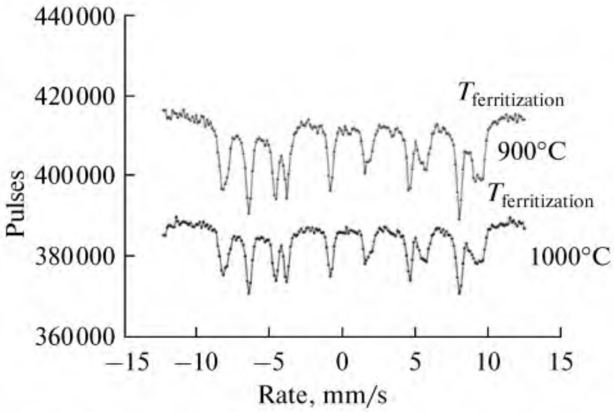

Fig. 9. Mossbauer spectra of hexaferrite specimens doped with barium.

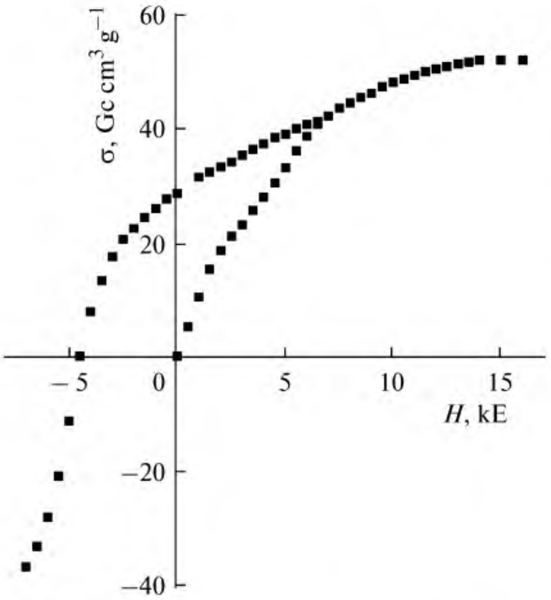

Fig. 10. Measurements of specific magnetization σ(*H*) of the specimen of microdispersed calcium hexaferrite doped with lanthanum.

It should be noted that the theoretical value of H_c for single-domain defectless noninteracting particles is $H_c \cong 0.48(H_a - H_{is}) \cong 6000$ E, where H_a is the field of magnetocrystalline anisotropy and H_{is} is the field of shape anisotropy.

The observed difference is related mainly related to lower anisotropy due to the negative contribution of surface anisotropy and, to some extent, the effects of interparticle magnetic interaction.

The measured magnetic properties of the $Ba_{0.5}Ca_{0.5}Fe_{12}O_{19}$ powder, i.e., the coercive force H_c = 2700 E (300K) and the shape of the magnetization curve, correspond to the system of multidomain particles or conglomerated microcrystals and are likely to be improved by modifying granulometric characteristics of the material.

CONCLUSIONS

A fine-grained magnetic material is synthesized based of calcium hexaferrite doped with lanthanum using a cryochemical technology at the stage of a salt precursor. Its structural and magnetic properties are investigated. The material particles are plate-shaped in the form of hexahedrons (or have a shape close to it), i.e., their shape is characteristic for hexaferrites. The particle distribution over the diameter (*d*) is within the micrometer range, i.e., the particle size corresponds to a single-domain state ($d \le 1.5$ μm), and the aspect ratio is d/h = 3–5 (where *h* is the particle thickness). The output magnetic parameters of synthesized microcrystalline powders doped with lanthanum are measured at 300°C and are H_c = 4500 E and σ_s = 47–42 G cm^3 g^{-1} (H = 18 kE).

The obtained value of H_c depending on the magnetic anisotropy of the interparticle magnetic interaction and the quality of crystals corresponds to those of the best microcrystalline systems of barium hexaferrite.

The synthesized material is characterized by high magnetic parameters and, as a result of the applied cryogenic technology, is chemically pure and homogeneous, which makes it possible to use it as medicine.

ACKNOWLEDGMENTS

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