

Chapter 2

Effects of Ultrasonic Synthesis Variable on Basic Properties of CoFe_2O_4 Nanoparticles

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2.1 Introduction

Recently, the interest in the development of new methods for the production of ferrite dispersed particles is increasing. This is due to their unique magnetic and electrical properties. Cobalt ferrite is a promising material because of its high crystallographic anisotropy, high coercivity, moderate saturation magnetization, chemical resistance, thermal stability and wear resistance [1–4]. Cobalt ferrite is used in magnetic recording, ferrofluid technology, biotechnology, medicine, biology, etc. [5–8].

Technological properties of cobalt ferrite are largely determined by the way it was received. Ceramic methods require large energy inputs and high-temperature synthesis. Thus, obtained ferrites are coarse. They have unstable composition and corresponding anion impurities. Therefore hydrophase synthesis methods are developing nowadays. The most modern are co-precipitation [9, 10], hydrothermal method [11, 12], method of reverse micelles [13], sol–gel [14], mechanosynthesis [15] and high-energy technologies [16–19]. Hydrophase methods allow to adjust the composition, crystallinity and morphology of the particles.

All of these methods have been studied by many researchers and successfully applied for the synthesis of cobalt ferrite. Precipitation methods usually comprise several stages. The first is precipitation, while the second is direct synthesis of

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ferrite, carried out by oxidation, ageing, etc. Recently scientists started to initiate the second main step of ferrite production, for example, using such oxidizing agents as KNO_3 or H_2O_2 . During ultrasound treatment, the solution flows through a set of complex chemical reactions involving radical particles and free electrons.

The major ultimate products of these interactions are oxygen, hydrogen peroxide and hydrogen. Oxidative activity of “activated” solutions can be used in the synthesis of complex oxide compounds.

The unique properties of ultrasound were used for the synthesis of complex inorganic compounds [20–23], for example, the sonochemical decomposition of volatile metal organic precursors for the preparation of cobalt ferrite. Sonochemical synthesis of ferrites is considered in the article [21]. Such materials have a wide range of biomedical applications, including their use as echo contrast agents for ultrasonic diagnosis, magnetic resonance imaging as well as oxygen or drug delivery. The impact of acoustic cavitation creates unique conditions of high energy to chemical reactions in the preservation of low-temperature liquid. Sonochemistry possibilities have been studied in the synthesis of unusual inorganic and biomedical materials. The authors of [22] have carried out a study on the magnetic properties of cobalt ferrite nanofluids under the influence of ultrasonic vibrations. In [23] the effects of pH and the composition of precursor intensity ultrasound treatment on the properties of cobalt ferrite derived from citrate solution were studied. Cobalt ferrites were prepared by combining the sol–gel method and ultrasonic irradiation. The pH values ranged from 5 to 9. In the present work, we studied the phase formation in the system Fe^{2+} – Co^{2+} – SO_4^{2-} – OH^- under the influence of ultrasonic vibrations. The variety of possible reaction products require additional study of the impact of frequency, pH and the intensity of exposure.

Our research of solution ultrasonic processing showed that the composition of the synthesized compounds is dependent on a wide range of factors [20, 24]. Using US processing provides a high degree of homogeneity in the distribution of components in the initial solution and in the ferrite formed during the oxidation. This contributes to effective interaction between them to form a homogeneous structure and composition of the compounds. We studied the process of nanoscale cobalt ferrite production at various pH.

2.2 Methodology of the Experiment

Production of co-precipitated compounds was carried out by pouring under continuous stirring the appropriate mixture of sulphate solutions with the required ratio of cations as in the ferrite. We used 0.5 M solutions of iron and cobalt salts. Polyhydrocomplex sol obtained at different pH was treated with ultrasound in a laboratory setup (Fig. 2.1). pH range is 7–12, period – 1.

It consisted of a ceramic reaction vessel, in which the ultrasonic dispersant transmitter USDN–2T was immersed and connected to the generator of ultrasonic vibrations. We investigated the influence of ultrasound at a frequency of 22 kHz and

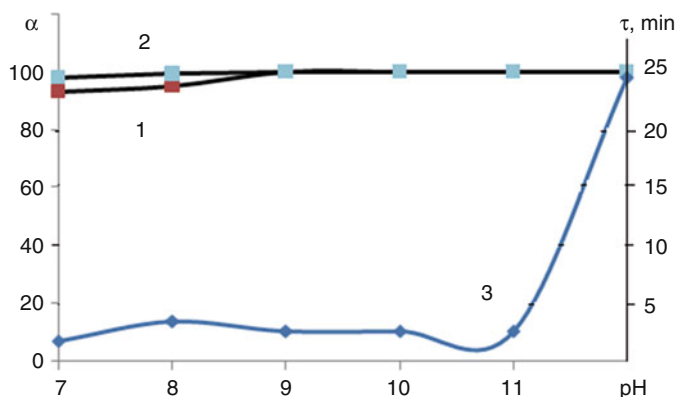


Fig. 2.1 Dependence of the degree precipitation of cobalt cation (1) and iron cations (2) and complete oxidation time (3) on the pH

the ultrasonic intensity at the load within 1 MW/m^2 . The optimal treatment time was selected in accordance to a plan drawn up previously.

The study of the phase composition of the samples was carried out using X-ray diffractometer DRON – 2.0 in $\text{Cu-K}\alpha$ monochromatic radiation. Scanning was performed at room temperature in the angle range of $5\text{--}85^\circ$, period = $0,04^\circ$.

The microstructure of the nanoparticles obtained was investigated by scanning microscopy with a help of Remme-102 microscope. The study of the magnetic properties of cobalt ferrite nanopowders was performed by vibrating magnetometry.

2.3 Results and Discussion

Possible mechanisms including the most probable processes that occur in the cavitation bubble were described by many researchers [20, 25, 26]. The basic idea of the ultrasonic treatment is based on cavitation effect.

As a result of passing through powerful acoustic wave cavitation, bubbles arise in the liquid, in which pressure and temperature are growing strongly. Thus electric discharges and explosions are generated, which lead to various physical and chemical processes that are not observed in other conditions [24].

During the processing of dispersion, medium crystalline precipitate is formed. Its disperse and phase composition is heavily dependent on the mode of the oxidation process: the nature of the oxidant, the oxidation rate, temperature, pH, oxidation start, the concentration of the precipitating agent and initial salt solution.

Kinetic curves showed that, under the influence of ultrasound, the pH of the sol will decrease due primarily to the oxidation of Fe^{2+} cations to Fe^{3+} (Fig. 2.1). The study of pH change differential curve made US possible to set the time of complete

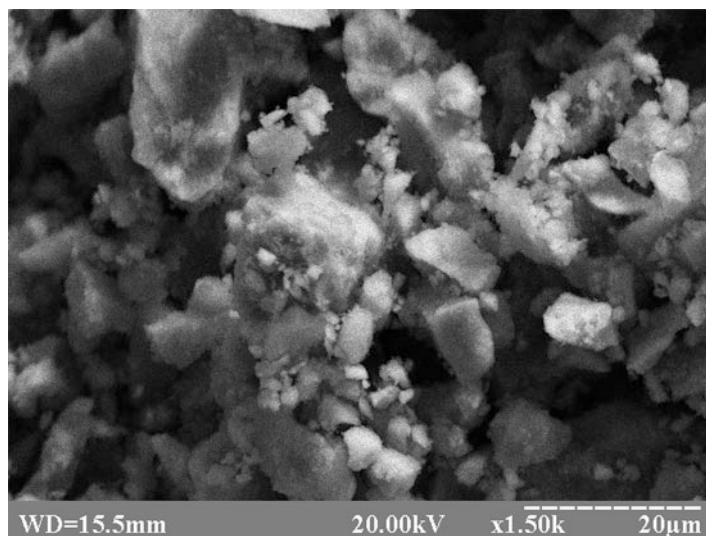


Fig. 2.2 CoFe_2O_4 powder microphotograph

oxidation. Decreasing pH causes partial dissolution of the precipitate, which affects the degree of precipitation (Fig. 2.2).

The extent of cobalt cation precipitation for pH 7 and 8 amounted 98.14 and 99.2, respectively; iron ions are present in the filtrate for pH 7 and 8 (the degree of precipitation was 93.23 and 95.2, respectively). In pH range of 9–12, almost complete precipitation of cobalt and iron cations takes place. Optimum pH can be considered as the value at which the relationship makes a straight line parallel to x axis.

It is known that the phase composition formed during the ultrasonic processing of products can be diverse.

Variable valency of the starting materials used in the synthesis and the oxidizing medium yield suggest the possibility of formation of undesirable phases of mixed oxyhydroxide, solid solutions of maghemite, lepidocrocite, goethite, hydrated oxides, etc. To assess the influence of ultrasound, it is necessary to define composition and properties of the resulting products during the ultrasonic treatment. According to experimental data, the oxidation process time with pH increasing in the range of 7–11 remains constant and then abruptly increases.

Figure 2.3 shows a typical microphotograph of cobalt ferrite sample prepared at pH = 12. The powder represents separate particles and irregular-shaped and different-sized faceted composites of agglomerated particles. Particle size analysis of the powder showed a great variation of particles sizes. Agglomerate size ranges within 1–20 mm. Thus there is particle shape anisotropy.

X-ray diffractions are shown in Figs. 2.3 and 2.4.

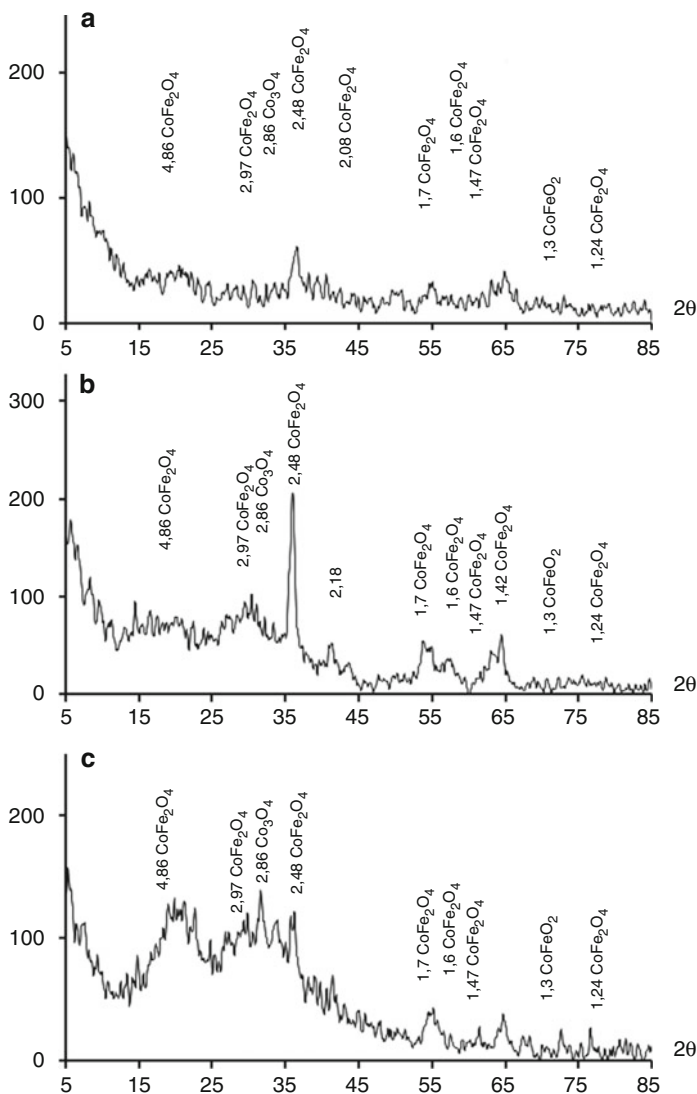


Fig. 2.3 X-ray diffraction pattern of samples obtained at different pH. **a-7, b-8, c-9**

The above-mentioned X-ray diffractions show only reflections corresponding to the spinel crystal lattice of cubic symmetry, which corresponds to JCPUS-22-1086 (Fig. 2.4c) and $\gamma\text{-(CoFe)}_2\text{O}_3$ and $(\text{CoFe})_3\text{O}_4$. The values of the lattice parameter a calculated from the XRD spectra were 0.83941 ± 0.00011 (Fig. 2.4c).

At low pH, amorphous phase is observed which is explained by the non-completion of the crystallization process. With increasing pH, the degree of crystallinity also increases. However, abnormally low values pH of coercive force

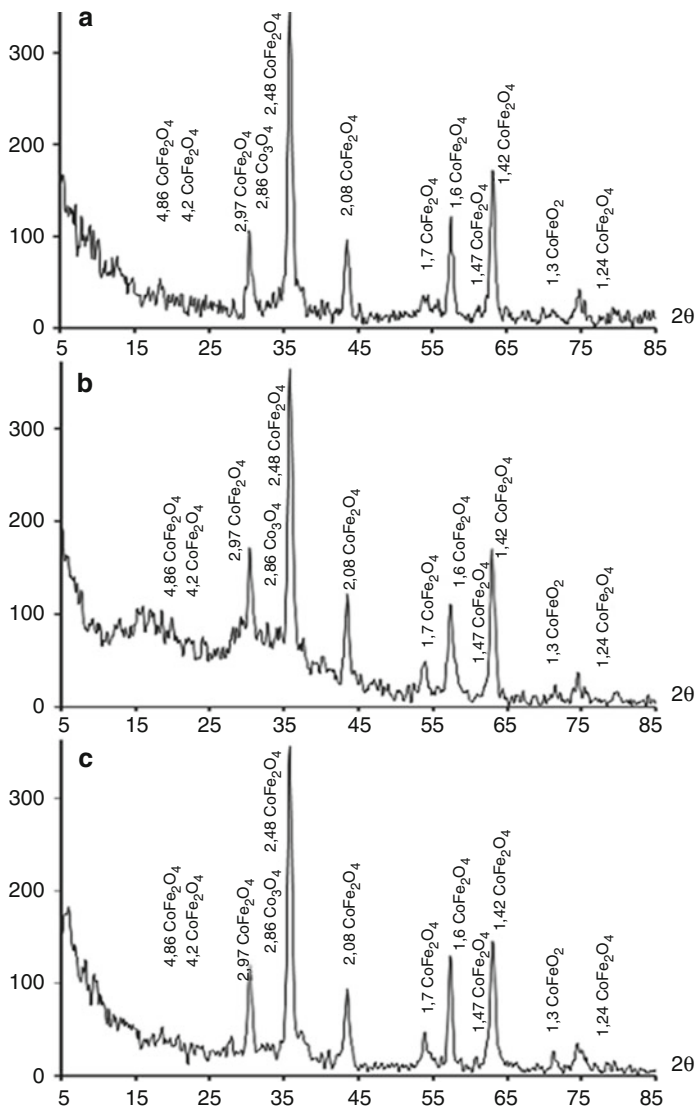


Fig. 2.4 X-ray diffraction pattern of samples obtained at different pH. **a**-10, **b**-11, **c**-12

at pH = 9 – 10 can be associated with the formation of maghemite crystal structure with integrated cobalt cations.

At pH = 12, cobalt ferrite is formed, which is confirmed by the magnetic measurements. Similar structure and similar reflections make it difficult to conduct quality identification with the help of X-ray analysis. Figure 2.5 shows magnetization measurement samples obtained at different pH. As follows from the figure, all

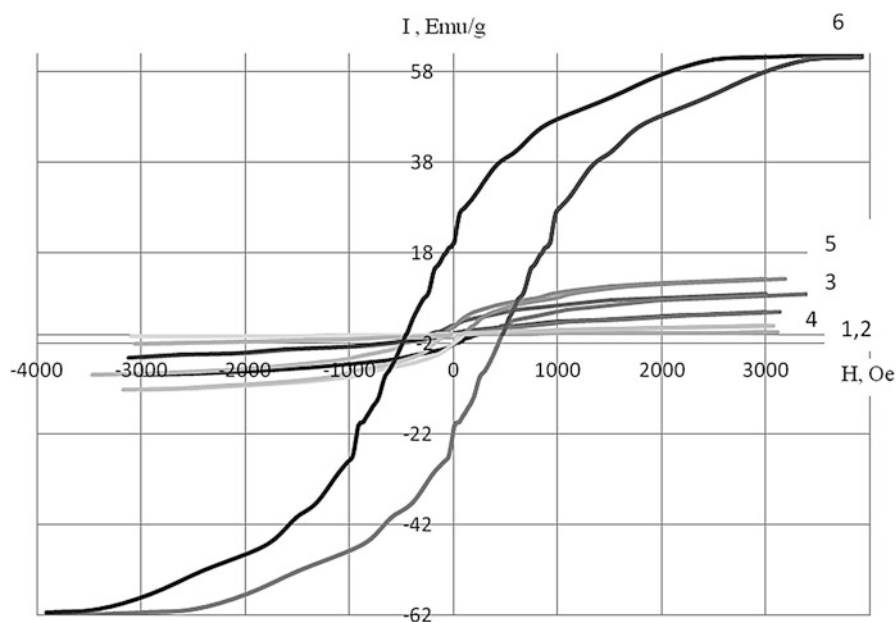


Fig. 2.5 Magnetization curves at room temperature of the samples prepared at pH. 1-7, 2-8, 3-9, 4-10, 5-11, 6-12

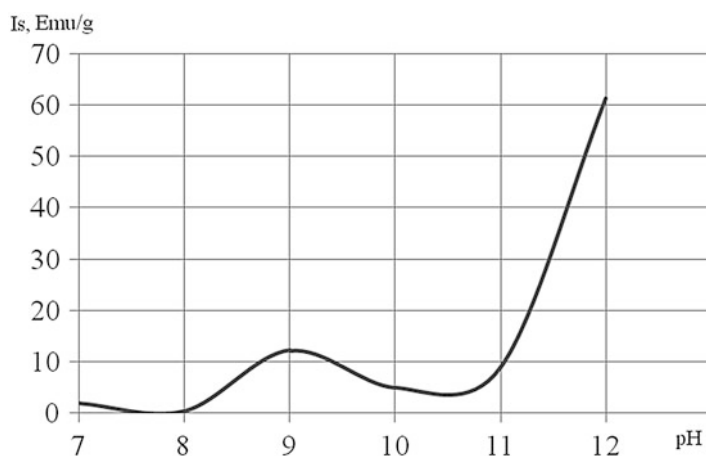


Fig. 2.6 The dependence of the coercive force on the pH

the samples in a magnetic field have saturation magnetization and hysteresis loop (Figs. 2.6 and 2.7).

The magnetic properties of cobalt ferrite are largely determined by the presence of superparamagnetic relaxation, which is represented in nanostructured systems. However, the presence and expression of the specific properties of nanodispersed

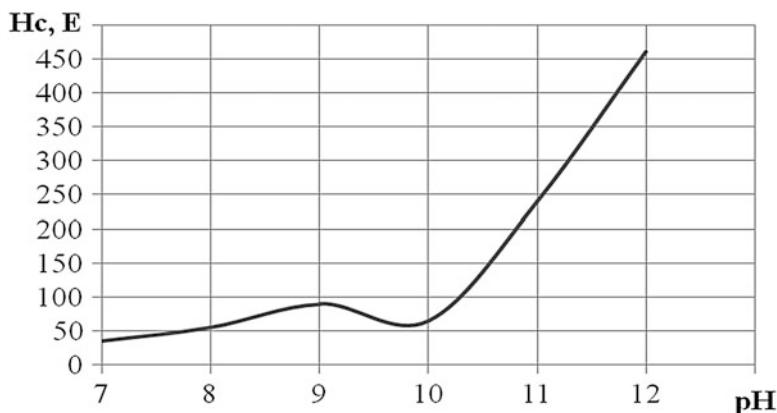


Fig. 2.7 Dependence of the saturation magnetization on the pH

materials are associated with the appearance of the magnetic dipole interaction between nanodisperse particles and magnetic field.

Saturation magnetization of the samples ranges from 0.5 to 59 emu/g. Coercive force, respectively, accounted for 50–450 Oe, which is correlated with the numbers shown in [5, 27]. It is known that fine ferromagnets possess specific magnetic properties. In this case, particle sizes of 1–20 mcm commensurate with magnetic domain boundary thickness. In this case, the boundary of the magnetic domain is larger than the magnetostatic energy of a single-domain particle, i.e. particles without boundaries. In this case, particles of such sizes do have boundaries, and they are called single-domain particles. In ferromagnets, consisting of such single-domain particles, magnetization can only take place by rotation of the magnetization vectors of individual particles. The value of the coercive force increases and is close to the theoretical value.

Comparative analysis of the nature of magnetic saturation curves and coercive force has shown a correlation of graphs 1, 6 and 7. This is primarily due to the fact that the magnetic characteristics are determined by the composition of the compounds formed.

The sequence of phases of formation can be represented as follows: $\gamma\text{-(CoFe)}_2\text{O}_3 \rightarrow (\text{CoFe})_3\text{O}_4 \rightarrow \text{CoFe}_2\text{O}_4$.

2.4 Conclusion

The studies established the conditions for obtaining fine particles CoFe_2O_4 under the influence of ultrasound. It is found that the particles have a faceted shape with an average size of agglomerates of 2–20 μ and a developed surface.

XR analysis showed that, depending on the pH synthesis, particles have different structures of crystal lattice of spinel cubic structure. The sequence of phases of formation can be represented as follows: $\gamma(\text{CoFe})_2\text{O}_3 \rightarrow (\text{CoFe})_3\text{O}_4 \rightarrow \text{CoFe}_2\text{O}_4$. Measurements of the magnetic properties of powders confirmed the stated assumption. Saturation magnetization (M_s) of samples ranged from 1.5 to 58 emu/g; coercivity (H_c) was 45–450 Oe depending on synthesis conditions.

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