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Natural and thermally stimulated aging of nanosized powders of cobalt ferrospinel

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Abstract. This article presents the production of nanosized powders of cobalt ferrospinel through mechanochemical synthesis, resulting in an average particle size ranging from 3 to 15 nm. The elemental composition of the nanopowders, analyzed using *X*-ray fluorescent analysis, is found to be nonstoichiometric and can be represented by the formula: $Co_{0.7\pm0.05}Fe_{2.3\pm0.05}O_4$. When the duration of mechanochemical synthesis exceeds 25 min, the spinel phase constitutes approximately 90 vol. % in the samples. Additionally, the samples contain hematite phases, the beta modification of iron hydroxide, and an *X*-ray amorphous phase. Natural aging at room temperature leads to significant changes in the phase composition of the nanopowders. Specifically, there is an increase in the content of spinel phase, while the content of hematite and the amorphous phase decrease significantly. Furthermore, the saturation magnetization and effective field of anisotropy of the cobalt ferrospinel nanopowders exhibit noticeable increments. Consequently, thermal aging of the powders accelerates the changes in phase composition, structural parameters, and magnetic properties, as well as enhances the transformation extent during the formation of cobalt ferrospinel.

Keywords: mechanochemical synthesis, cobalt ferrospinel, nanopowders, natural aging, thermally stimulated aging, magnetic anisotropy

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Естественное и термостимулированное старение наноразмерных порошков феррошпинели кобальта

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Аннотация. Методом механохимического синтеза получены наноразмерные порошки кобальтовой феррошпинели со средним размером частиц в интервале 3–15 нм. Элементный состав нанопорошков, исследованный методом рентгеновского флуоресцентного анализа, нестехиометрический и соответствует формуле $Co_{0,7\pm0,05}Fe_{2,3\pm0,05}O_4$. При времени механохимического синтеза 25 мин и выше содержание шпинельной фазы достигает 90 об. %, в образцах также присутствуют фазы гематита, бета-модификации гидроксида железа и рентгеноаморфной фазы. В результате естественного старения при комнатной температуре фазовый состав нанопорошков существенно меняется: увеличивается содержание шпинельной фазы, а гематита и аморфной фазы уменьшается в несколько раз. Также заметно возрастают намагниченность насыщения и эффективное поле анизотропии нанопорошков кобальтовой феррошпинели. Таким образом, термостимулированное старение порошков существенно ускоряет процессы изменения фазового состава, структурных параметров и магнитных свойств и увеличивает степень превращения при образовании феррошпинели кобальта.

Ключевые слова: механохимический синтез, кобальтовая феррошпинель, нанопорошки, естественное старение, термическое старение, магнитная анизотропия

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Introduction

Mechanochemical synthesis involves the mechanical processing of solid mixtures, leading to various processes such as substance disintegration, accelerated mass transfer, homogenization of mixture components, and activation of chemical interactions among solid reagents. The utilization of mechanical grinding in planetary high-energy mills has proven to be an effective method for producing powders, including magnetic powders, with microcrystalline unit sizes reaching as low as 10 nm or even lower. This approach facilitates the acceleration of interactions between nanocrystalline particles, which becomes particularly significant in the synthesis of multicomponent systems. In such cases, both mechanical and chemical forces come into play within the contact area between particles [1–9].

Finely dispersed magnetic powders with the particle sizes up to 10 nm garnered significant attention from researchers [10]. The small sizes of these powders and their unique properties make them suitable for targeted delivery of genetic material and medications to injured organs, enhancing magnetic resonance imaging contrast and other applications [11].

However, nanosized magnetic powders suffer from agglomeration, which tends to increase as the particle size decreases. Ultrasonic treatment in a liquid phase has proven effective in mitigating this drawback. It is worth noting that extended operation or storage leads to changes in physicochemical properties, commonly referred to as aging.

The phenomenon of aging in ferromagnetic materials exhibits universal characteristics. A study [12] investigated universality in various nonequilibrium lattice models with second-order phase transitions. Experimental data obtained from systems quenched from a high-temperature state at the critical temperature were utilized.

The exponent of the autocorrelation function and the asymptotic value of the dissipation coefficient were identified as universal variables. Monte Carlo simulation were conducted to analyze these universal variables in different lattice models.

Aging effects were further examined in [13; 14] for a specific case involving behavior of multilayer magnetic structures. The study revealed that aging effects occur not only during nonequilibrium critical behavior at $T = T_c$, (where T_c represents the critical temperature of ferromagnetic ordering) but also in wide temperature range with $T \le T_c$. In such magnetic structures, such as films with nanosized layers, an increase in the relaxation time results in deceleration of correlation and relaxation properties. These effects must be considered in the development and utilization of various magnetic structures.

Subsequent research by these authors [15] focused on calculating the temperature dependencies of equilibrium magnetic resistance values for a multilayer structure Co/Cu(100)/Co with varying thicknesses of cobalt magnetic layers. The theoretical results exhibited good agreement with experimental data, indicating an increase in the magnetic resistance coefficient in accordance with magnetic laws as temperature decreases and cobalt layer thickness increases.

The relaxation behavior of magnetization in the magnetic superstructure Co/Cu was investigated in [16]. The authors' analysis demonstrated that the relaxation behavior follows the pattern of full aging. The relaxation index, as a function of temperature, reveals distinct abnormalities during the equilibrium phase transition from an antiferromagnetic superstructure to paramagnetic layers.

Significant interest lies in studies examining the influence of aging on ferromagnetism in hydrogen-induced magnetic semiconductors with high Curie point [17]. It is known that these compounds exhibit a substantial increase in magnetization at 300 K after hydrogenation, particularly in cobalt- and iron-doped ZnO. The induced magnetization in paramagnetic ZnCo(5 %)O and ZnFe(5 %)O granules largely diminishes during storage due to material degradation.

In most cases, aging in materials is caused by decomposition of oversaturated solid solutions [18]. Depending on how the crystalline lattice constant changes, decomposition mechanisms can be categorized as continuous or discontinuous. Single-phase decomposition occurs when only one set of X-ray reflections from lattice of the initial solid solution is observed, while discontinuous decomposition involves a dropwise change in the lattice constant and the appearance of multiple sets of X-ray reflections.

In massive ferromagnetic materials undergoing single-phase aging, a single Curie point is observed, and its position gradually shifts with aging. In the case of two-phase aging, two Curie points exist, but one of them diminishes over time [18].

This study explores the influence of natural aging (at ambient temperature) and thermally stimulated aging (resulting from annealing at different temperatures) on the chemical and phase compositions, structural parameters, and key magnetic properties of nanosized powders of cobalt ferrospinel.

Experimental

In order to synthesize cobalt ferrospinel nanoparticles, the following reaction was employed:

$$2FeCl_3{\cdot}6H_2O + CoCl_2 + Ca(OH)_2 + 3Na_2CO_3 =$$
$$= CoFe_2O_4 + CaCl_2 + 6NaCl + 3CO_2\uparrow + 7H_2O.$$

The initial reagents used were of high purity, including pure, chemically pure, and pure for analysis grades. Furthermore, an inert component, sodium chloride, was added to the system in weight ratio of $m_{\text{r.m.}} : m_{\text{NaCl}} = 1{:}2$. This addition aimed to reduce the heating degree of reacting mixture (r.m) and thereby prevent particles aggregation in the final product. Subsequently, the system comprising the initial reagents and the inert component was placed in steel quenched barrels of a planetary mill with water cooling (acceleration: 60g). The ball to powder weigh ratio was maintained atc 20:1. The duration of mechanical processing or mechanochemical activation was varied between 5 and 60 min.

After the completion of mechanic activation, the resulting final product was extracted from the planetary mill barrels, washed with distilled water using a centrifuge (ROTANTA 430R, «Hettich», Germany) until all salts were completely removed, and dried at room temperature.

Natural aging of the cobalt ferrospinel nanosized powder was achieved through maturation in an exicator for 25 and 10,000 h, while thermally stimulated aging was conducted in an electric furnace over a temperature range of 100–600 °C for 60 min.

The chemical and phase compositions, morphology, dispersity, structure parameters, and magnetic properties of the cobalt ferrospinel nanopowders were analyzed following the procedures outlines in references [19–21].

Result and discussion

Electron microscopy images of cobalt ferrospinel nanoparticles and a histogram depicting the distribution of particle sizes can be found in references [20; 22]. The analysis revealed that the nanoparticles, ranging in size from 3 to 15 nm, exhibit a spherical shape and tend to aggregate weakly.

These results were corroborated and validated at the Engelgardt Institute of Molecular Biology, Russian Academy of Sciences (Moscow) during an investigation into the impact of cobalt ferrite magnetic particles on the spatial arrangement of DNA molecules [20]. By utilizing specially prepared suspensions and electron microscopy, the authors determined the average nanoparticle size to be within the range of 4.0 to 6.5 nm, consistent with the previously obtained results at the Tomsk Scientific Center, Siberian Branch, Russian Academy of Sciences. Furthermore, it was observed that the cobalt ferrospinel nanoparticles tend to form aggregates. Structural analysis using small-angle X-ray scattering indicated that the distribution of nanoparticle sizes encompasses particles with radii in the ranges of both 1 to 4 nm and 5 to 15 nm, which aligns with the observations made in reference [20].

The elemental composition of the synthesized nanosized powders of cobalt ferrospinel conforms to the formula $Co_{0.7\pm0.05}Fe_{2.3\pm0.05}O_4$. In addition to the main components, the powder contains impurities of manganese up to 0.15 wt. % and chromium up to 0.3–0.4 wt. %, which originated from the wear of steel balls. Consequently, X-ray fluorescent analysis demonstrated that the chemical composition of cobalt ferrospinel deviates significantly from its stoichiometric composition.

Figure 1 depicts the phase composition of cobalt ferrospinel as a function of the duration of mechanochemical processing.

For short duration of processing, the samples exhibit significant heterogeneity. Alongside the spinel phase, the presence of hematite and the beta modification of iron hydroxide phase is observed, along with approximately 10 % of X-ray amorphous phase. However, as the processing duration reached 25 min and beyond, the volume fraction of the spinel phase increases and stabilizes at around 90 %.

In order to assess the effects of natural aging, the structural and magnetic properties of cobalt ferrospinel were compared immediately after synthesis (within one day) with those after being held at ambient temperature for approximately 14 months (over 10,000 h). Table 1 provides a summary of the phase composition and structural properties of cobalt ferrite during natural aging.

During the maturation process of the nanopowders for over 10,000 h, a significant transformation in the phase composition is observed. The aged product no longer contains any traces of the hematite phase or the beta modification of iron hydroxide phase (β-FeO(OH)). Additionally, the content of the amorphous phase decreases substantially, from 3.0 to 1.0 vol. %, while the main product, the spinel phase, increases to 99 vol. % (refer to Table 1). The lattice constant of the nanopowders experiences a slight decrease, and the elastic microstresses, which are initially very high after mechanochemical synthesis of the nanosized powders, exhibit a reduction. The average particle size only changes by a maximum of 5–9 %.

Table 2 summarizes the magnetic properties of the synthesized nanopowders. The specific saturation magnetization (σ, $Gs \cdot cm^3/g$) is estimated using two methods. In the third column, the magnetization is determined by linear extrapolation of the high field segment of σ(*H*) to zero magnetizing field ($H \rightarrow 0$), while in the fourth column, it is determined by extrapolating $\sigma(H^{-1})$ to its value at $H \rightarrow \infty$.

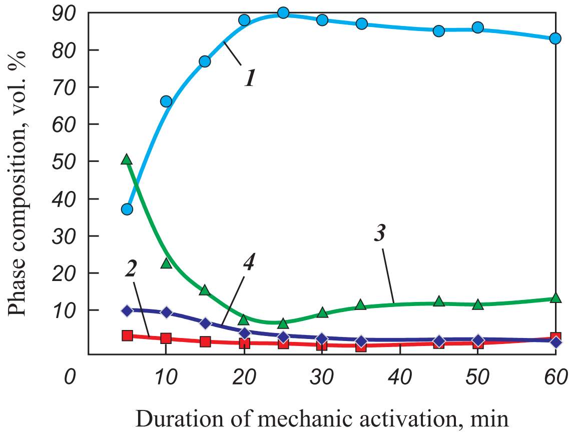

Fig. 1. The phase composition of cobalt ferrospinel as a function of the duration of mechanochemical synthesis
1 – cobalt ferrospinel, ***2*** – α-Fe_2O_3,
3 – β-FeO(OH), ***4*** – amorphous phase

Рис. 1. Зависимость фазового состава от продолжительности механохимического синтеза для кобальтовой феррошпинели
1 – кобальтовая феррошпинель, ***2*** – α-Fe_2O_3,
3 – β-FeO(OH), ***4*** – аморфная фаза

The effective fields of magnetic anisotropy (H_A) are determined by studying the second derivative of the magnetization curve, σ(*H*), following the procedure outlined in reference [21]. The effective constants of magnetic anisotropy (K_{eff}) for the materials under consideration are calculated using the equation:

$$H_A = \frac{2K_{eff}}{M_S},$$

where $M_S = \sigma\rho$ represents the saturation magnetization of unit volume in A/m and ρ denotes the specific weight of the synthesized powders in N/m^3.

The specific magnetization of the nanopowders and the field intensity of effective magnetic anisotropy experience significant changes during 10,000 h natural aging period at ambient temperature. The magnetization of the aged samples increases by approximately 14 % for cobalt ferrospinel (refer to Table 2). This increase in magnetization exceeds what can be attributed solely to changes in phase composition resulting from the transformation of nonmagnetic amorphous phase and antiferromagnetic hematite into the spinel phase.

It is plausible to assume that this effect is associated either with a decrease in the thickness of the nonmagnetic ("dead") surface layer of the ferrospinel nanoparticles or with a substantial reduction in the defect structure of the nanoparticle's crystalline structure upon aging. Notably, during natural aging, the value of the effective field of anisotropy for cobalt ferrospinel increases significantly. This increase can be attributed to the magnetic anisotropy primarily formed by the contribution of Co^{2+} ions, which exhibit a strong spin-orbital interaction (see Table 2).

Thermal processing can greatly stimulate diffusion processes responsible for changes in phase composition, structural parameters, and magnetic properties in nanosized ferrimagnetic powders. Therefore, in this study, powders of cobalt ferrite obtained with varying durations of mechanochemical processing were subjected to homogenizing annealing at temperatures of 100, 300 and 600 °C.

Table 1. **The influence of aging at ambient temperature on phase composition and structural properties of cobalt ferrospinel**

Таблица 1. **Влияние продолжительности старения при комнатной температуре на фазовый состав и структурные параметры кобальтовой феррошпинели**

Aging duration, h	Phase composition, vol.%				Lattice constant *a*, nm	Average particle size*, nm		$\Delta d/d$, 10^{-3}
	Spinel	Hematite	β-FeO(OH)	Amorphous phase		TEM	XSA	
25	90.0	1.0	6.0	3.0	0.8376	8.5	9.2	8.8
> 10,000	99.0	–	–	1.0	0.8370	–	9.6	7.2

* According to transmission electron microscopy (TEM) and *X*-ray structural analysis (XSA).

Table 2. **The influence of aging and annealing temperature on basic magnetic properties of cobalt ferrospinel**

Таблица 2. **Влияние продолжительности старения и температуры отжига после синтеза на основные магнитные характеристики кобальтовой феррошпинели**

Annealing temperature, °C	Aging duration, h	Specific magnetization σ, Gs·cm^3/g		H_A, Oe	$K_{eff}\cdot10^5$, erg·cm^3
		$H\to0$	$H\to\infty$		
20	25	22.3	36.1	1740	2.07
20	10,000	31.0	41.4	2300	1.75
100	25	55.4	–	1750	–
300	25	60.6	–	2500	–
600	25	58.8	–	4250	–

Figure 2 depicts the relationship between the content of the spinel phase, average sizes of crystallites, internal elastic microstresses, and specific saturation magnetization for cobalt ferrospinel. It presents these parameters as a function of both the duration of synthesis and the annealing temperature.

Annealing at a temperature of 100 °C has a minimal impact on the structural properties of cobalt ferrospinel. It primarily results in a slight increase in the content of the spinel phase. However, at higher annealing temperatures, there is a notable increase in the average particle size and a significant (around 3–5 times) reduction in the internal elastic microstresses. These changes in structural parameters subsequently have a substantial effect on the magnetic properties of ferrimagnetic nanopowders.

Table 2 provides a summary of the main magnetic properties, including the specific saturation magnetization and the effective field of magnetic crystallographic anisotropy, for nanosized powders of cobalt ferrite. These properties are analyzed in relation to the duration of mechanochemical synthesis and various modes of thermal processing.

The increase in magnetization is most pronounced in samples synthesized in less than 25 min. This increase can be attributed to the growth in average particle size, leading to a reduction in the relative volume of the "dead" surface layer and a decrease in the extent of the defect structure within crystallites. The dependences of the effective field of magnetic anisotropy are more complex, as they involve a competition between volumetric and surface anisotropy, as well as contribution of magnetoelastic interactions.

Changes in the effective field of magnetic anisotropy of cobalt ferrospinel nanoparticles upon aging warrant individual discission. As reported in [23], the effective

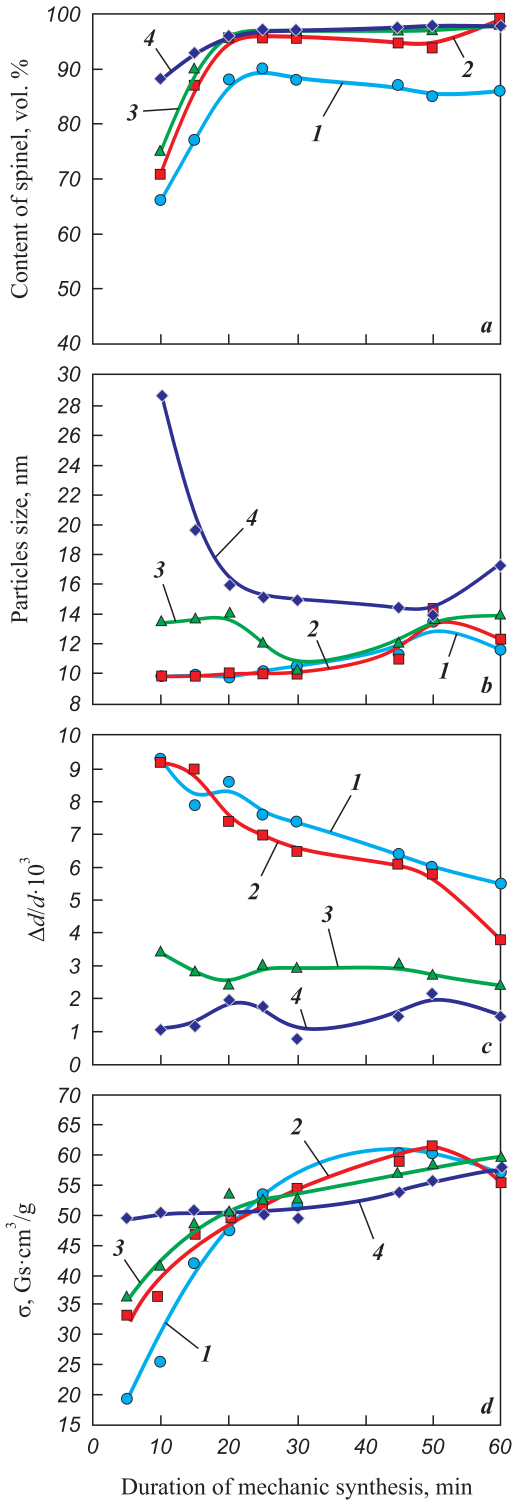

Fig. 2. The content of the spinel phase (***a***), average particle size (***b***), internal elastic microstresses (***c***) and saturation magnetization (***d***) as a function of mechanochemical synthesis time and subsequent heat treatment temperature
1 – t = 20 °C, ***2*** – 100 °C, ***3*** – 300 °C, ***4*** – 600 °C

Рис. 2. Зависимости содержания шпинельной фазы (***a***), среднего размера частиц (***b***), внутренних упругих микронапряжений (***c***) и намагниченности насыщения (***d***) от продолжительности механохимического синтеза и температуры последующей термической обработки
1 – t = 20 °C, ***2*** – 100 °C, ***3*** – 300 °C, ***4*** – 600 °C

constant of magnetic anisotropy of the nanoparticles can be expressed as the sum of the following components:

$$K_{eff} = K_{\text{MKA}} + \lambda_S \sigma = \left(1 - \frac{V_S}{V_V}\right) K_V + \frac{V_S}{V_V} K_S + \lambda_S \sigma,$$

where the first and the second terms account for the contributions of volumetric and surface magnetocrystalline anisotropies, respectively, while the latter term represents the contribution of magnetoelastic interactions. Here K_V and K_S denote the constants of anisotropy for the internal volume and surface layer, respectively; λ_S is the coefficient of ferrimagnetic magnetostriction; $\sigma = (\Delta d/d)E$ represents the value of internal elastic microstresses, where E is the Young modulus; V_S is the volume of the excited surface layer; V_V is the non-excited internal volume.

Considering the negligible changes in the sizes of ferromagnetic particles during natural aging, the field changes, and hence the effective constant of anisotropy, are primarily governed by the decrease in internal elastic microstresses with aging. This implies a change in the contribution of the magnetoelastic component to the total energy of crystal anisotropy. Consequently, the magnetostriction coefficient for nanosized powders of ferrimagnetic compounds can be estimated using the following equation

$$\lambda_S = \delta H_{\text{A}} \frac{M_S}{2E} \delta \frac{\Delta d}{d},$$

where δH_{A} denotes the change in the field of magnetic anisotropy during aging.

The magnetostriction constant obtained for cobalt ferrite nanoparticles is $68 \cdot 10^{-6}$, which is approximately half the value observed for massive crystals. It should be noted that estimating such values for materials after annealing is problematic due to difficulties in separating the contributions of surface anisotropy and magnetoelastic interactions.

Table 3. **The chemical composition of cobalt ferrospinel nanopowders as a function of the duration of mechanochemical activation**

Таблица 3. **Влияние времени активации нанопорошков кобальтовой феррошпинели на ее химический состав**

Duration of mechanic activation, min	Content, at. %		Chemical formula
	Fe	Co	
10	43.34	23.04	$Co_{1.04}Fe_{1.96}O_4$
20	48.95	17.94	$Co_{0.80}Fe_{2.2}O_4$
30	14.73	48.94	$Co_{0.69}Fe_{2.31}O_4$

Therefore, nanosized powders of oxide ferrimagnetic materials produced through mechanochemical synthesis exist in a metastable state and tend to transition into a stable state during aging at ambient temperature. The evolution of phase composition, structural parameters, and magnetic properties provides evidence of relaxation processes upon aging.

One such processes is crystallization of the amorphous phase, although its influence on changes in phase composition and magnetic properties is minimal due to its negligible content compared to the spinel phase. Regarding hematite, its absence after aging is likely due to its dissolution in the spinel phase.

X-ray fluorescent analysis of the elemental phase of the synthesized samples revealed that, in all cases after mechanochemical synthesis, the concentrations of components do not correspond to their stoichiometric ratio (Table 3). Furthermore, the cubic lattice is maintained, with a lattice constant lower than that of materials in bulk form, and the elastic stresses are very high.

It can be hypothesized that over prolonged aging, hematite undergoes dissolution in the spinel phase through solid-phase diffusion under high stress conditions. Consequently, the chemical composition of the ferrimagnetic material approaches stoichiometry. Substantial evidence supporting this notion includes a notable increase in specific saturation magnetization and alterations in the effective field of magnetic anisotropy. The primary processes governing the changes in magnetic properties of nanosized powders during thermally stimulated aging are the reduction in the significance of the surface layer and the extent of magnetic defect structure.

Conclusions

1. It has been experimentally shown that cobalt ferrite nanoparticles synthesized through mechanochemical methods using iron chloride (III) crystallohydrate exhibit weak agglomeration, a spherical shape, and sizes in ranging from 3 to 15 nm. The elemental composition of the synthesized nanopowders is non-stoichiometric and can be described by the formula: $Co_{0.7\pm0.05}Fe_{2.3\pm0.05}O_4$.

2. *X*-ray fluorescent analysis (XFA) reveals significant changes in the phase composition of cobalt ferrite nanopowders during aging (>10,000 h after synthesis at ambient temperature):

– the content of the desired product (spinel phase) increases to 99.0 vol. %;

– no impurity phases of hematite and iron hydroxide are detected;

– the final product after aging only exhibits traces of an amorphous phase.

3. Both natural and thermally stimulated aging result to an increase in the average particle size and a significant decrease in internal elastic microstresses (indicating a reduction in the defect structure of cobalt ferrite nanopowders).

4. Aging is accompanied by a significant increase in saturation magnetization due to an increase in the content of the ferrimagnetic phase and a decrease in the fraction of the surface "dead" layer and the defect structure of the ferrimagnetic material.

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V. I. Itin – determined the purpose of the work, participated in the discussion of the results, wrote the manuscript.

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