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Low-Temperature Mossbauer Studies of the Phase Composition and Structural Stability of Iron (III) Oxide/Hydroxide Nanocomposite

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In article present the results of low-temperature Mossbauer studies of iron (III) oxide/hydroxide nanocomposite synthesized by the method of deposition. Based on these studies, the composition of the synthesized composite was revealed. The nanodispersed composite with a specific surface 280 m²/g is a hematite in the weakly disordered crystalline state (CSR 10 nm), and a lepidocrocite in the X-ray amorphous state (particles size 3 - 4 nm). The relative integral intensity of the Zeeman sextet, which corresponds to the magnetically ordered phase of hematite, is practically unchanged and is about 17%. The tendency to divide the magnetically ordered component into two sextets, which differ in quadrupole splitting $Q_S = -0.21$ mm/s and $Q_S = 0.21$ mm/s, respectively, is observed starting from a temperature of 190 K. As a result of annealing of the synthesized material at a temperature of 200 °C, a slight redistribution (≈ 5 %) of the content of paramagnetic and magnetically ordered components was recorded, which indicates the structural stability of the nanoparticles of the lepidocrocite γ -FeOOH phase at this temperature. Increase of annealing temperatures to 500°C leads to the predicted course of the phase transition γ -FeOOH \rightarrow α -Fe₂O₃. The mechanism of growth of hematite crystallites during sintering due to fixation side faces of larger α -Fe₂O₃ phase of nanoparticles of the γ -FeOOH phase with simultaneous transformation of their crystal structure to side faces of larger α -Fe₂O₃ phase particles is presented.

Keywords: iron (III) oxide/hydroxide nanocomposite, Mossbauer, magnetically ordered and paramagnetic components, Zeeman splitting, effective magnetic field.

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Introduction

Problems of phase composition identification and modification of crystal structure of nanoscale materials is extremely relevant at present [1, 2]. It is especially true of nanoscale materials obtained by liquid-phase methods of "green chemistry" [3], because their great advantage is high energy efficiency and morphological variability. However, a significant disadvantage from using liquid-phase deposition is the residual content of structurally bound molecules of H₂O and OH⁻ groups in the synthesized materials. In most cases, they are present in the structure of nanomaterials in the form of the corresponding amorphous crystal hydrates and

hydroxides, which cannot be identified by X-ray diffraction methods [4].

In the synthesis of nanosized iron compounds by chemical deposition methods, a precipitate consisting of amorphous aggregates of about 100 nm in size is precipitated during the formation of the iron hydrogel. They are formed from uncrystallized so-called "primary particles" with sizes below 3 - 4 nm. As established by the authors [5-7], the change of key parameters of the synthesis in a fairly wide range is: – the pH of the reaction medium from 4 to 14, the temperature of the solutions from 20°C to 100°C, the concentration of solvents 0.5 – 6 M practically weren't affect the size of "primary particles". The question about of the phase composition of

the "primary particles" is remains open. In most cases, prepared precipitate is considered suitable for $\text{Fe}(\text{OH})_3$. However, $\text{Fe}(\text{OH})_3$ is an unstable phase as a result to the zero value of amount of energy cause of formation with Fe_2O_3 and H_2O . Therefore, it is advisable to consider the iron hydrogel as a three-dimensional polymer of variable composition $x\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Thus, the "primary particles" are the nuclei of micelles of the formed colloid-polymer. The polymer structure of the nuclei is unstable because it is formed at the time of strong supersaturation of the solution during deposition. Aging of "primary particles" in the mother liquor causes their depolymerization and next transformation into centers of crystallization of secondary crystals, which can be phases of hematite or goethite.

The aim of this work is low-temperature Mossbauer studies of the phase composition and structural stability of nanosized systems of iron (III) oxide/hydroxide nanocomposite obtained according to the method of chemical deposition proposed in [7]. The synthesis of materials involved the crystallization of "primary particles" outside the mother liquor and the preservation of their initial size of the order of a few nanometers.

I. Materials and methods

The method [7] was used for synthesis of sample. This method involve the precipitation of iron hydrogel, which was previously received by mixing aqueous solutions of FeCl_3 and NaOH with a given value of $\text{pH} = 7$ at a temperature of 20°C . Dehydration of the precipitate was performed in air for 4h at a temperature of 110°C .

Diffraction patterns were obtained with a DRON-3.0 (Cu $K\alpha$ radiation, Bragg-Brentano geometry and a Ni $K\beta$ -filter). For studying the crystal and magnetic microstructure, the method of low temperature (88 - 290 K) Mossbauer spectroscopy was used: an MS-1104Em device, the constant-acceleration regime, the Co^{57} isotope in a chromium matrix serving as a source of γ quanta, the line width of metallic α -Fe equal to 0.21 mm/s, and the calibration of isomeric shifts with respect to α -Fe. The morphology of samples was studied by transmission electron microscopy (TEM) with a 100 kV microscope JEOL JEM-100CX II. Thermal analysis was performed using a STA 499 F3 Jupiter in a argon atmosphere in the temperature range of 25 - 1000 $^\circ\text{C}$ and a heating rate of $5^\circ\text{C}/\text{min}$. The samples surface area was measured by the Brunauer-Emmett-Teller (BET) method using an Quantachrome Autosorb (Nova 2200e) device with nitrogen as adsorbate. The adsorption isotherms were measured at 77 K.

II. Results

In Fig. 1 presents the results of X-ray diffraction analysis. The obtained diffraction pattern for the synthesized material indicates its X-ray amorphous state. Only minor traces of the main most intense reflexes (104) and (110) of the weakly crystallized phase of hematite are recorded. The particle size of this X-ray component of the material, according to the construction of Williamson-

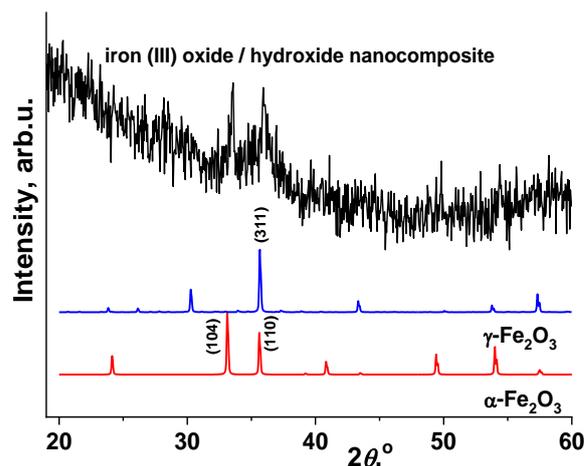


Fig. 1. X-ray diffraction pattern of synthesized iron (III) oxide / hydroxide nanocomposite and model patterns of crystal structure of maghemite (JCPDS Card No. 39-1346) and hematite (JCPDS Card No. 33-0664).

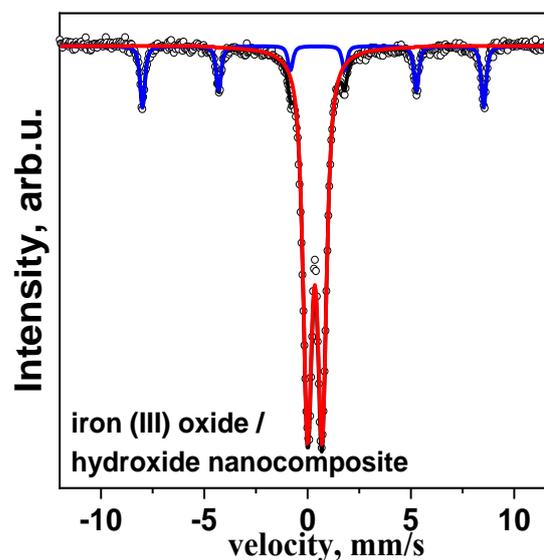


Fig. 2. Mossbauer spectrum of synthesized iron (III) oxide / hydroxide nanocomposite and decryption components obtained by using the software Univem MS 7.01.

Hall, is about 10 nm. In fact, these nanoparticles form a magnetically ordered component on the Mossbauer spectrum, the relative content of which is $\approx 17\%$ (Fig. 2). The characteristic parameters of the Zeeman sextet $H_{\text{ef}} = 513$ kOe, $I_S = 0.37$ mm/s and $Q_S = -0.22$ mm/s unambiguously confirm their belonging to the hematite phase. There is also a high-intensity paramagnetic component on the spectrum, the content of which is $\approx 83\%$.

The high degree of dispersion of the obtained system is indicated by the value of the specific surface area of the material measured by the method of isothermal nitrogen adsorption, which is $S_{\text{sp}} = 280$ m^2/g . This is also confirmed by the obtained TEM image of the sample (Fig. 3), according to which the average size of the formed

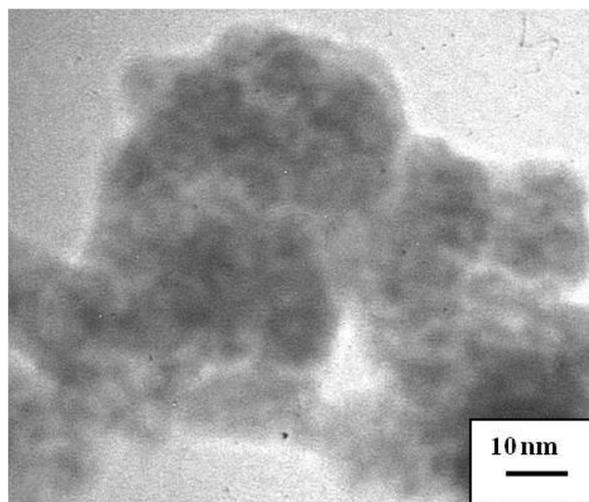


Fig. 3. TEM image of synthesized iron (III) oxide / hydroxide nanocomposite.

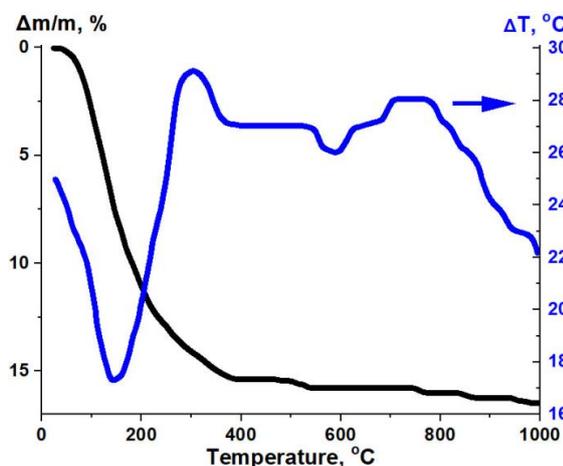


Fig. 4. Thermogravimetric analysis of synthesized iron (III) oxide / hydroxide nanocomposite.

dominant particles is about 3 - 4 nm.

To clarify the phase composition of the material, thermo-gravimetric studies of the obtained material were performed (Fig. 4). It was found that in the temperature range from room to 360°C, the sample loses about 15 % of its mass, and the intensity of mass loss is maximum in the range from 20°C to 200°C. This process corresponds to the recorded endothermic maximum in the vicinity of a 150°C. Thus, it is highly probable that the paramagnetic component is formed by resonant Fe^{57} nuclei, which are part of one of the modifications of the FeOOH phase. The calculated mass losses of this phase during dehydration with the formation of hematite are about 10 %, and during the formation of the FeO compound -19 %.

To confirm the fact of formation of the FeOOH phase and to establish its modification, low-temperature Mossbauer spectroscopy (MS) of the study of the synthesized sample was used (Fig. 5).

It is established that at all applied cryo temperatures in the range from room temperature to liquid nitrogen temperature the relative integral intensity of the Zeeman sextet, which corresponds to the magnetically ordered phase of hematite with particles of 10 nm, remains

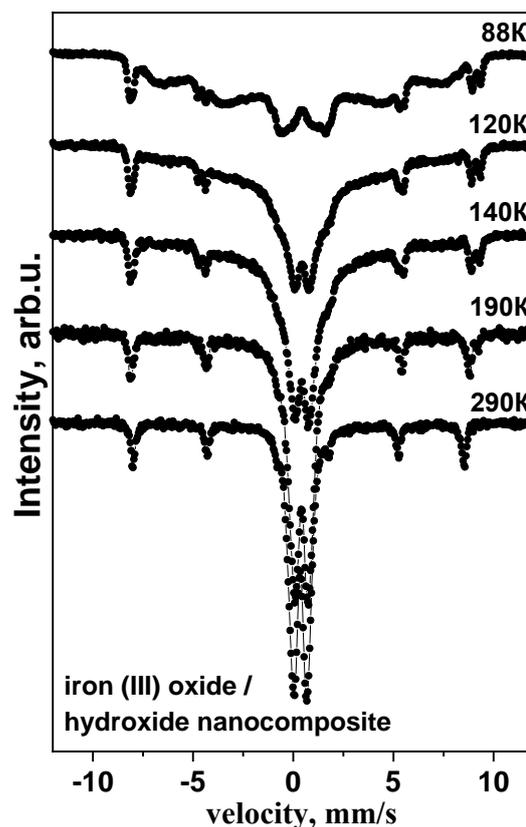


Fig. 5. Low-temperature Mossbauer spectra of synthesized iron (III) oxide / hydroxide nanocomposite obtained at different cryo temperatures.

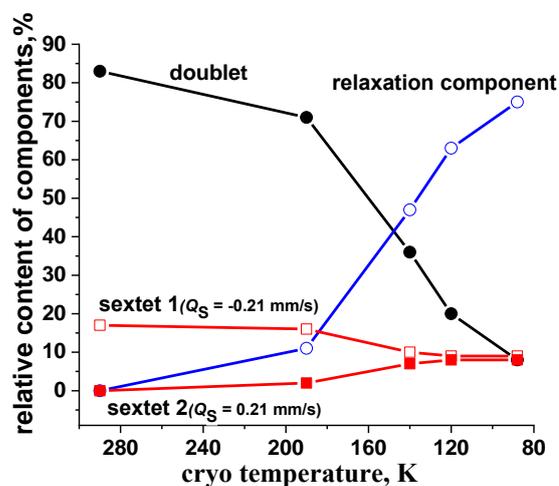


Fig. 6. Dependence of relative integral intensities of the main components of the Mossbauer spectra of synthesized iron (III) oxide / hydroxide nanocomposite on the cryo temperature of measurement and removing degenerate state for the magnetically ordered component.

practically unchanged and is about 17 % (Fig. 6). At the same time, starting from the temperature of 190°K, there is a tendency to divide this component into two sextets, which differ in the values of quadrupole splitting, respectively $Q_S = -0.21$ mm/s and $Q_S = +0.21$ mm/s. When using shooting temperatures of 120 K and 88 K, their contribution becomes almost commensurate. The

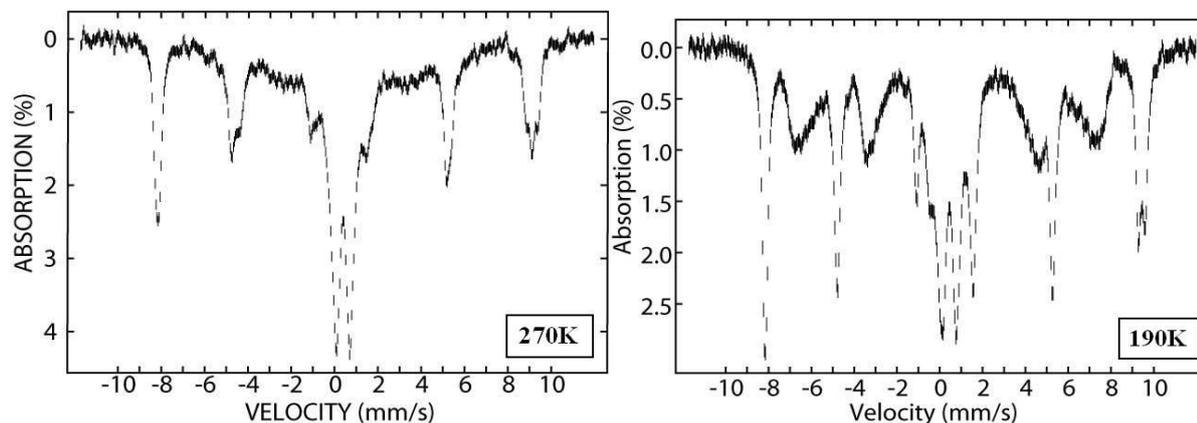


Fig. 7. Mossbauer spectra for the model mixture (1: 1) synthetic hematite ($<5\ \mu\text{m}$) and Silesian lepidocrocite (HMM 81159) [301] at temperature 270 K (left) and 190 K (right).

recorded result serves as another indisputable proof of the conformity of these components to the hematite phase.

III. Discussion

The obtained results were explained on the basis of the structure of the magnetic structure of this phase. Hematite is an antiferromagnetic in which two magnetic sublattices completely compensate for each other. There are slight deformation of the octahedras, which leads to quadrupole splitting with a value whose modulus is equal to 0.21 mm/s. However, the thermal oscillations of the lattice ions at room temperature do not allow to separate the contribution of these two magnetic lattices. The use of a cryo temperature of 120°K provides complete removal of the corresponding degeneracy with a clear fixation of two magnetic sublattices of hematite with antiparallel magnetic moments.

When the recording temperature decreases from 140°K, a significant redistribution of the relative integral intensities of the paramagnetic and relaxation components of the corresponding MS is also observed in the direction of increasing the latter (Fig. 6). The residual content of the paramagnetic component of the spectrum at a recording temperature of 88°K is 8 %. In this case, the relaxation component is a superposition of significantly expanded Zeeman sextet with the parameters $I_S = 0.39\ \text{mm/s}$, $Q_S = -0.26\ \text{mm/s}$. At the same time, the distribution of the values of effective magnetic fields on resonant nuclei in the range from 212 kOe to 446 kOe with maxima in the vicinity of $H_{\text{ef}} = 257\ \text{kOe}$, 359kOe and 437 kOe. The obtained result for the relaxation component is characteristic of the phase of lepidocrocite $\gamma\text{-FeOOH}$ with a Neel temperature of 77°K.

This is also confirmed by almost identical MS spectra registered in the Mars Mineral Spectroscopy Database, which were obtained for a model mixture containing synthetic hematite ($<5\ \mu\text{m}$) and Silesian lepidocrocite (HMM 81159) in the ratio to each other (Fig. 7) [8]. However, in our case, the phase of $\gamma\text{-FeOOH}$ is much more dispersed, because the formation of characteristic Zeeman components begins at significantly lower shooting temperatures in the range of 120 - 88 K. It should be noted that the spectrum of the model mixture, which is obtained

at a shooting temperature of 190°K, also, as in our case, the degeneration was recorded for the hematite phase with a clear fixation of the two magnetic sublattices.

To establish the degree of structural stability, the synthesized starting material was annealed in air at high temperatures in the range from 200°C to 500°C for 5 hours. The corresponding MS spectra of annealed samples of material are presented in Fig. 8.

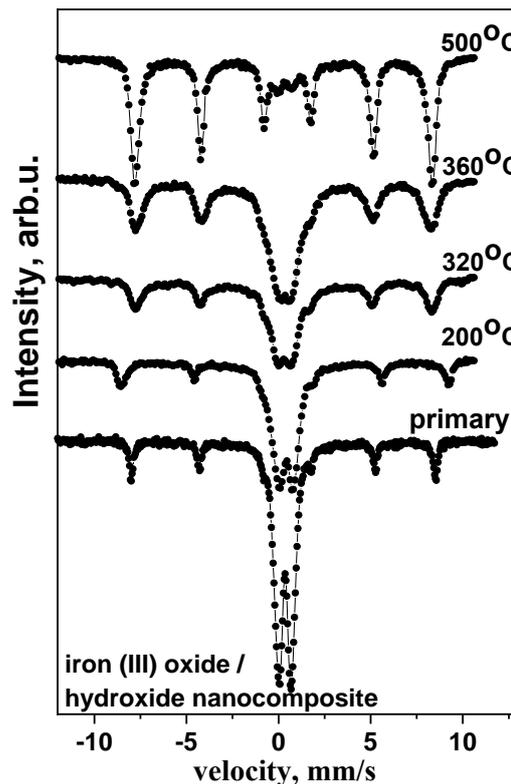


Fig. 8. Mossbauer spectra of synthesized iron (III) oxide / hydroxide nanocomposite after annealing at temperatures from 200°C to 500°C.

As a result, it was recorded that annealing at a temperature of 200 °C is accompanied by only a slight redistribution ($\approx 5\%$) of the content of paramagnetic and magnetically ordered components (Fig. 9). However, there is a significant increase in the value of the effective magnetic field of the corresponding Zeeman sextet of the

magnetically ordered component to 550 kOe (Fig. 9). The recorded results show that at a given annealing temperature the nanoparticles of the lepidocrocite phase γ -FeOOH are quite structurally stable and remain in their initial state with almost all their mass. At the same time, annealing of structural defects occurs in the microcrystallites of the hematite phase, which increases the degree of structural perfection of the latter and, as a consequence, increases the value of the effective magnetic field of the corresponding Zeeman component [9]. A further increase in the annealing temperatures to the selected, according to thermogravimetric studies (Fig. 4), characteristic values of 320°C, 360°C and 500 °C leads to the predicted course of the phase transition γ -FeOOH \rightarrow α -Fe₂O₃. The transition is long and the applied final annealing temperature of 500°C does not ensure the completeness of its course. The corresponding residual content of the paramagnetic component is 11 %.

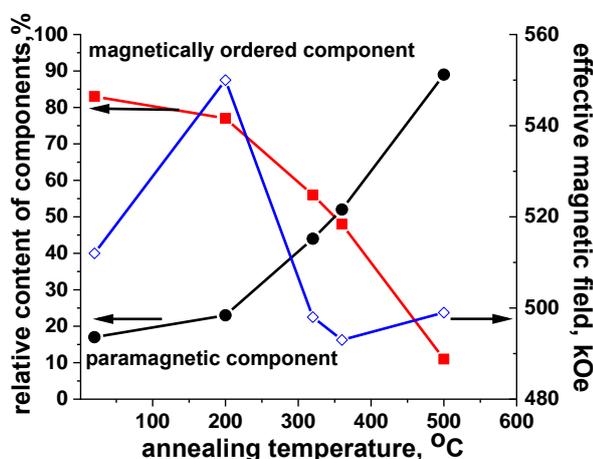


Fig. 9. Dependence of relative integral intensities of magnetically ordered and paramagnetic components of the Mossbauer spectra synthesized iron (III) oxide / hydroxide nanocomposite and effective magnetic field of the magnetically ordered component on annealing temperature.

It should be noted that the annealing process is characterized by the absence on the spectra of the corresponding samples of the relaxation component, which would indicate the direct conversion of γ -FeOOH nanoparticles into the corresponding α -Fe₂O₃ particles, followed by sintering and microcrystalline formation. In this case, there is a mechanism of growth of hematite crystallites due to the growth of nanoparticles of the γ -FeOOH phase with simultaneous transformation of their crystal structure to side faces of larger α -Fe₂O₃ phase particles. The value of the weighted average value of the effective magnetic field of the corresponding Zeeman sextet of the magnetically ordered component at the beginning of the phase transition decreases to the level of 498 kOe (Fig. 9) Due to the formation of defective intergranular regions in the crystallites during their growth and remains virtually unchanged throughout the

subsequent annealing process.

Conclusions

The structural and morphological characteristics, magnetic microstructure and structural stability of iron (III) oxide/hydroxide nanocomposite synthesized by the deposition method were studied. Low-temperature Mossbauer studies revealed that the composite material is a mixture of hematite nanocrystallites (\approx 10 nm) and nanoparticles of the lepidocrocite phase (3 - 4 nm). The specific surface area of the material is $S_{sp} = 280$ m²/g. For the hematite phase at cryo temperatures below 120 K, the existence of two magnetic lattices with antiparallel magnetic moments, which differ in the values of quadrupole splitting ($Q_S = -0,21$ mm/s and $Q_S = +0,21$ mm/s, respectively) was established.

It was established that at the annealing temperature of 200 °C of iron (III) oxide/hydroxide nanocomposite the nanoparticles of the γ -FeOOH phase are sufficiently structurally stable and all remain in the initial state. At the same time there occur an annealing of structural defects in nanocrystalline of the hematite phase. Due to this, there is an increase in the effective magnetic field of this Zeeman sextet of the magnetically ordered component to 550 kOe. A further increase in annealing temperatures to 500°C leads to a phase transition γ -FeOOH \rightarrow α -Fe₂O₃. According to the proposed model, the growth of hematite nanocrystallites occurs due to the addition of nanoparticles of the γ -FeOOH phase to the side faces of larger particles of the α -Fe₂O₃ phase and then transformation of their crystal structure. In this case, there is cannot direct conversion of individual nanoparticles of γ -FeOOH into the corresponding particles α -Fe₂O₃, because the content of the relaxation component on the Mossbauer spectra does not change. The effective magnetic field of the corresponding Zeeman sextet of the magnetically ordered component, which corresponds to the hematite phase, decreases to 498 kOe at the beginning of the phase transition and remains practically unchanged throughout the annealing process in the applied temperature range.

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Низькотемпературні месбауерівські дослідження фазового складу та структурної стійкості нанокompозиту оксид / гідроксиду заліза (III)

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В роботі представлено результати низькотемпературних месбауерівських досліджень нанокompозиту оксид / гідроксиду заліза (III), отриманого методом співосадження. На основі перехресних X-променевого аналізу та месбауерівської спектроскопії виявлено фазовий склад синтезованого нанодисперсного композиту, який складається із гематиту ($\alpha\text{-Fe}_2\text{O}_3$) у слабвпорядкованому кристалічному стані (ОКР ≈ 10 нм) та лепідокроциту ($\gamma\text{-FeOOH}$) у рентгенівському аморфному стані (розмір частинок 3 - 4 нм). Питома площа поверхні синтезованого нанокompозиту становить $280 \text{ м}^2/\text{г}$. На основі низькотемпературних месбауерівських досліджень виявлено зміни магнітної мікроструктури нанокompозиту. Зокрема, встановлено, що відносна інтегральна інтенсивність секстету, що відповідає магнітновпорядкованій фазі гематиту, практично не змінюється і становить близько 17 %. При цьому апроксимація магнітновпорядкованої компоненти, починаючи від температури 190 К, відображається двома секстетними лініями, які відрізняються квадрупольним розщепленням ($Q_S = -0,21 \text{ мм/с}$ і $Q_S = 0,21 \text{ мм/с}$). В результаті відпалу синтезованого нанокompозиту при температурі $200 \text{ }^\circ\text{C}$ зафіксовано незначний перерозподіл ($\approx 5 \%$) вмісту парамагнітних та магнітновпорядкованих компонентів, що свідчить про структурну стійкість наночастинок $\gamma\text{-FeOOH}$ при відпалі. Підвищення температур відпалу до 500°C призводить до прогнозованого перебігу фазового переходу $\gamma\text{-FeOOH} \rightarrow \alpha\text{-Fe}_2\text{O}_3$. Представлено механізм росту кристалітів гематиту під час спікання за рахунок фіксації на бічних гранях фази $\alpha\text{-Fe}_2\text{O}_3$ наночастинок фази $\gamma\text{-FeOOH}$ з одночасним перетворенням їх кристалічної структури на структуру фази $\alpha\text{-Fe}_2\text{O}_3$.

Ключові слова: нанокompозит оксид/гідроксиду заліза (III), месбауерівська спектроскопія, магнітновпорядкована та парамагнітна компоненти, Зеєменівське розщеплення, ефективне магнітне поле.