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SYNTHESIS AND MAGNETIC MICROSTRUCTURE OF NANOPARTICLES OF ZINC-SUBSTITUTED MAGNESIUM FERRITES

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Nano-sized magnesium-zinc powders are synthesized, by using the sol-gel autocombustion technology. On the basis of X-ray researches, the phase composition of non-magnetic substituted ferrite systems is determined. The resulting complex oxide powders are found to be agglomerated. The agglomerates consist of several nanoparticles with an average size of 18–32 nm. According to the cation distribution in magnesium-zinc ferrites, Zn^{2+} cations are found to occupy positions in the tetrahedral sublattice (A-sites) and displace Fe^{3+} cations into the octahedral sublattice (B-sites). The Mössbauer spectrum registered for the magnesium ferrite powder at room temperature shows two characteristic Zeeman sextets. For ferrites substituted with non-magnetic cations, the Mössbauer spectra are superpositions of several sextets and superposing doublets. The studies also show that the shape of Zeeman spectral lines depends on the particle size, which testifies to their superparamagnetic properties. The dependence of Mössbauer parameters such as the isomer shift, the quadrupole splitting, and the hyperfine magnetic field on the Zn^{2+} ion concentration is discussed. It is supposed that a change of the effective magnetic field with increasing the zinc content in magnesium-zinc ferrites is related to the fact that the substitution of Fe^{3+} cations by Zn^{2+} ones reduces the indirect exchange interaction between the A and B sublattices in ferrites with the spinel structure, which actually leads to their magnetic ordering.

Keywords: ferrite, nanoparticles, cation distribution, Mössbauer spectroscopy, superparamagnetism.

1. Introduction

Owing to their structural, physical, chemical, electric, and magnetic properties, spinel ferrites are very important objects, because they are widely applied in various domains of engineering [1]. In recent years, one of the leading directions in the modern materials science has been the synthesis of various substances with nanoparticles that possess given properties, as well as the creation of functional materials on their basis. Rather a large number of methods have been developed to synthesize nano-structured systems, which allow the dimensions and the shape of nanoparticles – and, accordingly, their physico-chemical properties – to be controlled. It is known that the structure and, hence, the properties of materials are

formed at the stage of their fabrication. It is evident that the choice of q technology to fabricate nanomaterials has a great value to provide their stable and optimum operational characteristics. The application of nanoferrites to the information storage, manufacture of microwave devices, and communication technology gradually increases [2], owing to unique magnetic properties of nanoparticles in comparison with those of massive crystalline materials with the same chemical composition.

The magnetic properties of spinel ferrite materials depend on interactions between the magnetic moments of cations located in the tetrahedral (A) and octahedral (B) sublattices [3]. Therefore, the study of magnetic properties of complex oxide systems with the spinel structure would be impossible without the study of their magnetic microstructure [4]. Undoubtedly, the substitution of magnetic cations by non-

magnetic ones should substantially affect the properties of ferrites. Moreover, owing to the ability of non-magnetic cations to occupy the sites in different spinel sublattices, those properties can be widely varied. In addition, the distribution of cations in ferrites depends on the method used in their synthesis, sintering temperature and atmosphere, stoichiometry, porosity, and size of substituting cations.

Magnesium-zinc ferrites are stable inexpensive magnetic semiconductors, which are widely used in electronics and telecommunication [5]. At present, large crystalline particles of those ferrites and their properties have already been studied. For example, the authors of work [6] analyzed the microstructure evolution in Mg-Zn ferrites obtained at temperatures from 900 to 1400 °C with the use of the ceramic technology. In the same work, the influence of the sintering temperature on the magnetic, electric, and mechanical properties of ferrites was studied. The variations in the saturation magnetization depending on the Zn²⁺ substitution degree were described in works [7] and [8], where magnesium-zinc ferrites were obtained, by using the ceramic and hydrothermal methods, respectively. The authors of work [9] analyzed the structure and the magnetic properties of Mg-Zn ferrite powders synthesized by the co-precipitation method.

However, the literature sources contain no information on the influence of substitution with Zn²⁺ cations in magnesium ferrites synthesized following the sol-gel autocombustion (SGAC) technology on their magnetic properties, which would be studied, in particular, on the basis of experimental data obtained with the help of the Mössbauer spectroscopy. Therefore, this work was aimed at the sol-gel synthesis of the powders of magnesium ferrites with a partial substitution with non-magnetic zinc cations and the research of their magnetic microstructure.

2. Experimental Technique

Ferrites Mg_{1-x}Zn_xFe₂O₄ with $x = 0.0, 0.2, 0.44,$ and 0.5 were synthesized with the help of the SGAC method [10]. The following chemical reagents were used for the synthesis: magnesium oxide (MgO), zinc oxide (ZnO), iron nitrate nonahydrate (Fe(NO₃)₃ · 9H₂O), citric acid (C₆H₈O₇ · H₂O), nitric acid (HNO₃), and distilled water. A high combustion rate was provided by selecting a molar ratio of 1 : 1 be-

tween metal nitrates and citric acid. The corresponding amount of each reagent was dissolved in 50 ml of water. With the help of a 25% ammonia solution and at permanent stirring, the pH level in the solution was made equal to 7. Then the solution was dried up at a temperature of 130 °C until its transformation into xerogel. Finally, owing to the autocombustion of dry gel, ferrite powders were obtained.

The phase composition of the powders was determined with the help of the X-ray diffraction method. X-ray patterns were registered at room temperature with the help of a diffractometer DRON-3 and with the use of the CuK_α radiation ($\lambda = 1.5419 \text{ \AA}$). Diffraction patterns were registered in a scanning range of 15°–65° with a step of 0.02°. The morphology of the powders obtained after the autocombustion was studied on a scanning electron microscope JEOL NeoScope JSM-5000. While determining the specific surface area and studying the porous structure of ferrite powders obtained with the use of the sol-gel technique, physical adsorption methods are used the most often [11]. This makes it possible to study such parameters as the specific surface area, the mesopore volume, and the distribution of pores over their dimensions. The specific surface area in magnesium-zinc powders was determined by analyzing the sorption isotherms of nitrogen at a temperature of 77 K on an automatic sorptometer Quantachrome Autosorb (Nova 2200e). It should be noted that the accuracy of this method amounted to ±10%.

Mössbauer absorption spectra of magnesium-zinc specimens were obtained at room temperature on a spectrometer MS-1104Em. As a source of γ -quanta, ⁵⁷Co with an activity of 100 mCi in a chromic matrix was used. Gamma quanta were registered with the help of a scintillation counter with a NaI crystal as a sensitive element. The resolution of experimental Mössbauer spectra into components was carried out by applying the universal program UnivemMS-7; namely, the spectra were approximated by sums of analytical functions describing separate components in the experimental spectrum. Isomeric shifts were calibrated with respect to metallic α -Fe.

3. Results Obtained and Their Analysis

3.1. Structural researches

Experimental X-ray diffraction patterns of the powders of the Mg_{1-x}Zn_xFe₂O₄ system obtained after

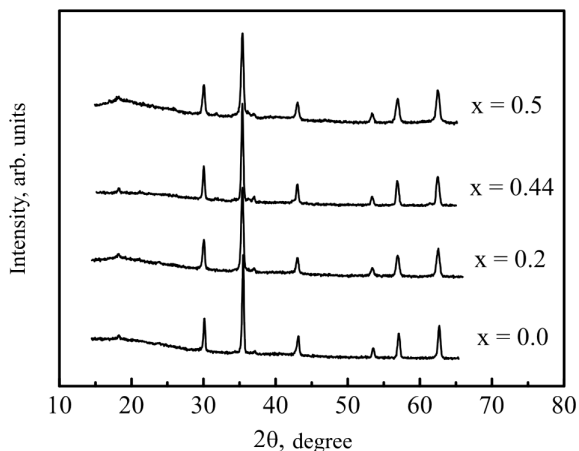


Fig. 1. X-ray diffraction patterns of magnesium-zinc ferrites

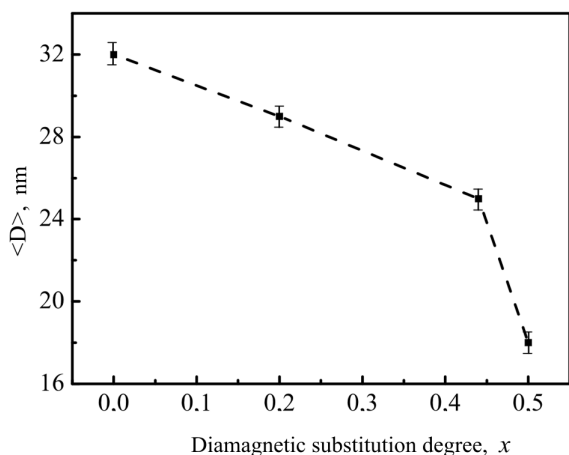


Fig. 2. Dependence of the average CSR size in magnesium-zinc ferrites on the Zn^{2+} content

their autocombustion are exhibited in Fig. 1. According to the analysis, the X-ray diffraction patterns of the powders obtained by the SGAC method testify to the cubic spinel structure of the spatial group $F3dm$.

The average size of coherent scattering regions (CSRs) in the powders of magnesium-zinc ferrites was found from the peak (311), by using the Scherrer equation

$$\langle D \rangle = \frac{0.9\lambda}{\beta \cos \theta}, \quad (1)$$

where β is the effective half-width of the diffraction peak for X-rays with wavelength λ at an angle θ . In work [12], while studying nickel-zinc ferrites, it was established that the presence of zinc in the speci-

mens made the process of crystal growth more complicated. The dependence of the CSR size in the obtained powders on the substitution degree with Zn^{2+} cations in magnesium ferrite is shown in Fig. 2.

However, when analyzing the powders of magnesium-zinc ferrites with the help of the scanning electron microscopy, particle accumulations were revealed, whose dimensions substantially exceeded those of CSRs determined by the X-ray diffraction analysis. The obtained result testifies that some of ferrite particles synthesized with the help of the SGAC method form agglomerates not bigger than 100 nm in dimensions. Therefore, the estimated CSR size can be identified with the dimensions of nanoparticles in the agglomerate. The agglomeration of particles is most likely associated with the presence of a magnetic interaction between them [9].

The analysis of the curve describing the dependence of the CSR size in the $Mg_{1-x}Zn_xFe_2O_4$ system on the Zn content x has shown that the average diameter of nanoparticles decreases as the content of Zn^{2+} cations increases. It is worth noting that the average dimensions of agglomerates also diminish at that. The growth of crystals in the course of powder synthesis is known to depend on various parameters, the most important of which is the cation distribution between the spinel sublattices.

Magnesium-zinc ferrites belong to the type of mixed ferrites. The corresponding structure is expressed by the formula $(Fe^{3+}_x Me^{2+}_{1-x})[Me^{2+}_{1-x} Fe^{3+}_x]$. Mixed ferrites, besides Fe^{3+} cations, also contain two more cation forms, which tend to occupy the same positions in the crystal lattice, as they occupy in the corresponding monoferrite. For example, in magnesium-zinc ferrites, Zn^{2+} cations have a tendency to occupy tetrahedral sites, and Mg^{2+} cations tend to octahedral ones [13]. As the fraction of spinel with the normal structure increases, the number of Fe^{3+} cations at tetra-positions decreases. The latter are displaced by Zn^{2+} cations into octahedral sites. However, deviations from those rules are possible, depending on the fabrication method and conditions.

The distribution of cations between the tetrahedral and octahedral sublattices in the structure of magnesium-zinc powders was determined with the help of the full-profile Rietveld method. The intensity of X-rays is affected by variations in the concentrations of Mg^{2+} , Zn^{2+} , and Fe^{3+} cations at the tetra- and octahedral lattice sites. For $3d$ -cations Zn^{2+} and

Fe³⁺, the factor of X-ray scattering is considerably larger than for 2p-cations Mg²⁺. Therefore, the magnitude of structural factor and the line intensity considerably depend on the variation in the concentration of Mg²⁺ cations in the corresponding crystallographic positions. The determination error for the cation distribution in the spinel structure amounted to ±0.01.

The obtained structural formulas for all examined powders are quoted in Table 1. It should be noted that Zn²⁺ cations expectedly occupy only A-sites and displace Fe³⁺ cations into B-sites, with an insignificant fraction of Mg²⁺ cations remaining in the tetrahedral sublattice. Since Mg²⁺ cations have an electron shell typical of inert gas atoms, their appearance in the A-sublattice was expected. On the other hand, the cation distribution in magnesium ferrites is sensitive to the temperature-time regime. In work [14], by analyzing the kinetics of the processes running at the synthesis of materials within the SGAC method, it was found that, after the autocombustion process has terminated, the rate of cooling of particles corresponds to the hardening regime. Therefore, it is probable that some of Mg²⁺ cations may have no time to occupy B-sites.

3.2. Mössbauer spectroscopy studies

Figure 3 demonstrates the Mössbauer spectra of Mg–Zn ferrites registered at room temperature. The Mössbauer spectrum of non-substituted magnesium ferrite reveals a superposition of two Zeeman sextets associated with the presence of iron cations in both the tetrahedral and octahedral lattice sites. This fact testifies to the ferrimagnetic character of the synthesized powder with the spinel structure. Such a spectrum is typical of substances obtained with the help of the ceramic technology or the annealing at temperatures higher than 600 °C [15].

The Mössbauer spectra for all other ferrite powders are superpositions of several Zeeman sextets. Note that the Mössbauer spectra for Zn²⁺-substituted powders do not demonstrate a pronounced cation distribution between the sublattices, which can be associated, probably, with the emergence of extra magnetically nonequivalent positions for Fe³⁺ cations in the B-sublattice as a result of their different surrounding by magnetic and non-magnetic cations belonging to the A-sublattice. Due to such changes in the envi-

ronment of magnetic iron cations induced by an increase in the concentration of Zn²⁺ cations in magnesium ferrites, the asymmetric broadening of Zeeman lines is possible. It should be noted that the asymmetric broadening of lines in the Mössbauer spectra of nanoparticles is typical of mixed spinels containing zinc cations [16].

The probability of the formation for magnetically nonequivalent Fe_A³⁺ positions is determined by the binomial distribution [17]

$$P(n) = \frac{z!}{n!(z-n)!} k^{z-n} (1-k)^n, \quad (2)$$

where z is the coordination number. This expression makes it possible to calculate the relative number of tetra-coordinated Fe³⁺ cations, for which n cations ($0 \leq n \leq 4$) of available four neighbor ones are magnetic, provided that the relative content of non-magnetic cations in the octahedral sublattice equals k .

In addition to the broadened relaxation sextet structure, the experimental Mössbauer spectra of magnesium-zinc ferrite powders also contain a doublet. According to Gilleo's model [18], a magnetic cation with two or less magnetic exchange bonds with cations in the other sublattice behaves as paramagnetic one and does not make a contribution to the total magnetization. Therefore, there is a discrete set of values for local fields at the iron nuclei, whose atoms occupy some magnetically nonequivalent sites in the octahedral lattice, which affect the broadening of lines in the Mössbauer spectrum. The calculated values of probabilities, $P(n)$, allowed us to predict the distribution of the relative intensities of partial Zeeman sextets in the Mössbauer spectra of all powders. Moreover, the probabilities for the environments with the number of the nearest neighbors not more than 2 were determined. If the calculated probabilities are assumed to correspond to the relative content of the paramagnetic component in the spec-

Table 1. Cation distributions in Mg–Zn ferrites

Zinc content, x	Cation distribution between the sublattices
0.0	(Mg _{0.22} Fe _{0.78})[Mg _{0.78} Fe _{1.22}]O ₄
0.2	(Mg _{0.21} Zn _{0.20} Fe _{0.59})[Mg _{0.59} Fe _{1.41}]O ₄
0.44	(Mg _{0.11} Zn _{0.44} Fe _{0.45})[Mg _{0.45} Fe _{1.55}]O ₄
0.5	(Mg _{0.11} Zn _{0.50} Fe _{0.39})[Mg _{0.39} Fe _{1.61}]O ₄

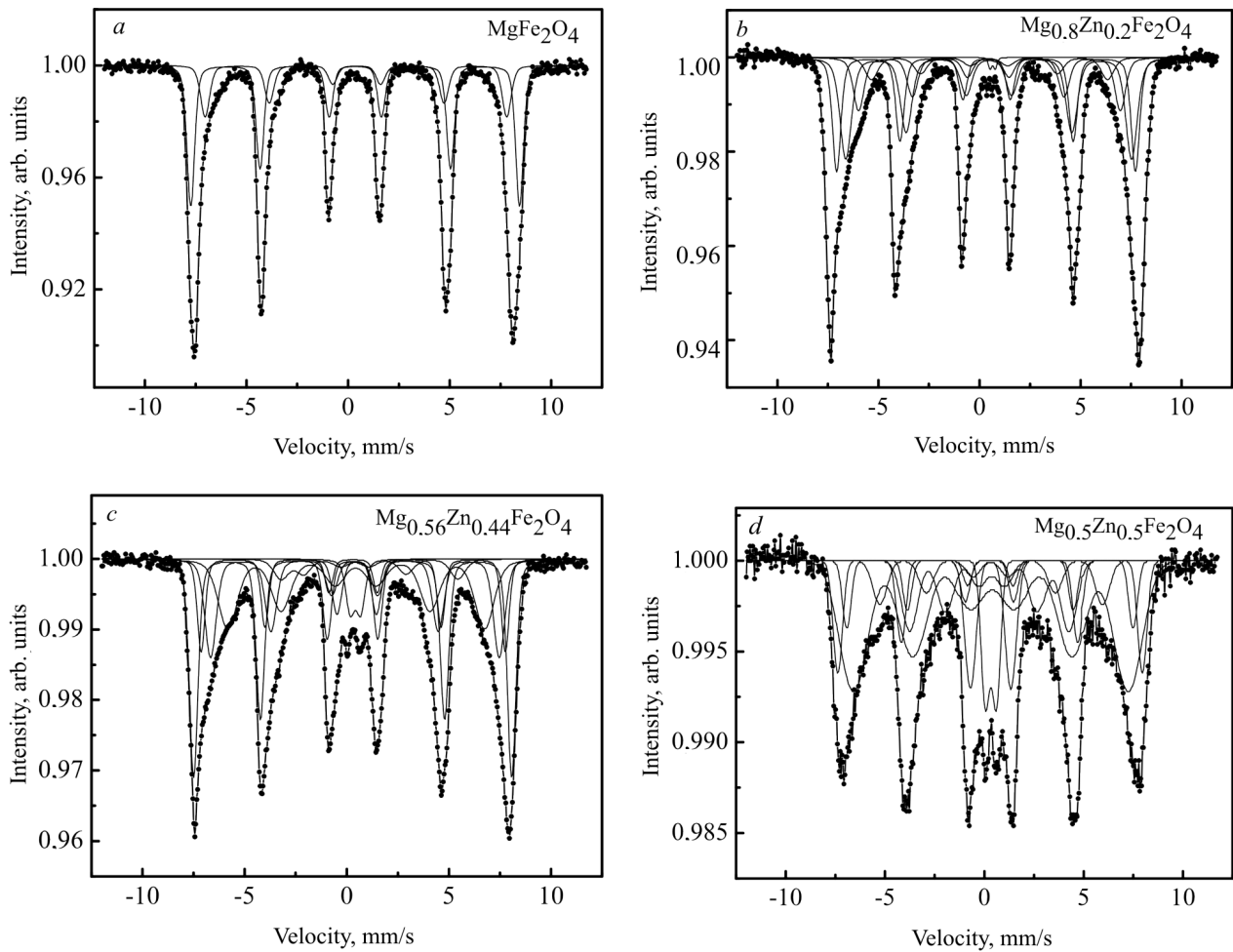


Fig. 3. Mössbauer spectra of powders of the $Mg_{1-x}Zn_xFe_2O_4$ system

trum, then, e.g., for the specimen with $x = 0.5$ the integrated intensity of the doublet component should be equal to about 0.4 and 2.9% at $n = 1$ and 2, respectively. However, having compared the calculated

Table 2. Results of Mössbauer spectroscopy researches of paramagnetic components in Mg–Zn ferrites

Zinc content, x	Component	δ , mm/s	Δ , mm/s	I , %
0.2	Doublet	0.47	0.85	2.3
0.44	Doublet 1	0.35	0.51	3.4
	Doublet 2	0.41	1.07	4.4
0.5	Doublet 1	0.28	0.56	7.0
	Doublet 2	0.32	1.24	8.3

values of integrated intensity with experimental ones, which amount to 7.0 and 8.3% (see Table 2), we may suppose that some part of the material is in the superparamagnetic state. Note that the relative integrated intensities I were determined making no allowance for different fraction values f (energy losses at the nucleus recoil). However, it cannot change the conclusion in principle. An alternative reason for the doublets, which are an attribute of the paramagnetic phase, to appear can be the presence of some iron cations in the near-surface layers of the examined particles, because the structural composition of those layers can substantially differ from that in the bulk.

On the other hand, the Mössbauer spectra of magnesium-zinc ferrite powders demonstrate an increase of the integrated intensity of the spectral component

corresponding to Fe^{3+} cations in the paramagnetic state, as the degree of substitution with Zn^{2+} cations grows. The obtained experimental data agree with the results of work [19]. There, the magnetic properties of magnesium-zinc ferrite powders with particles of various dimensions, which were obtained within the co-precipitation method, were studied. It was found that the spectrum for a $\text{Mg}_{0.15}\text{Zn}_{0.85}\text{Fe}_2\text{O}_4$ specimen with an average particle size of 6 nm contains a doublet, whose relative contribution decreases, as the dimensions of particles grows to 22 nm. Comparing this information with the experimental data obtained in our work, a conclusion can be drawn that manifestations of the superparamagnetism phenomenon can be responsible for the presence of the paramagnetic component in the spectra of synthesized powders.

Superparamagnetic relaxation is the most important feature in the Mössbauer spectra of nano-sized powders. The superparamagnetism arises, when the particles are so small that the thermal energy can overcome the energy of anisotropy and change the orientation of the magnetization of particles from one easy magnetization axis to the other one [20].

For very small particles with uniaxial anisotropy, the energy barrier that separates two directions of easy magnetization can even be lower than the thermal energy at room temperature. This circumstance results in spontaneous fluctuations of a magnetization direction with the relaxation time [11]

$$\tau = \tau_0 \exp\left(\frac{KV}{k_B T}\right), \quad (3)$$

where the parameter τ_0 weakly depends on the temperature and falls within the interval of 10^{-12} – 10^{-9} s, k_B is the Boltzmann constant, V the particle volume, T the temperature, and K the magnetic anisotropy constant. If the volume of a ferrimagnetic particle becomes smaller than a certain critical value, the domain structure of the particle becomes energetically unfavorable, so that it transits into the state of uniform magnetization. As a result, a system of single-domain particles with single-phase magnetization is formed. In this case, the distribution of spins corresponds to a minimum of the total magnetic energy.

A monodomain particle is registered by the Mössbauer spectroscopy method as a paramagnetic one, provided that the relaxation time τ of the magnetic moment is shorter than the lifetime τ_s of the excited state of Mössbauer nucleus ^{57}Fe . The lat-

ter equals 1.41×10^{-7} s, according to the data of work [21], and plays the role of the “time of observation” of the system in those experiments. Hence, the form of Mössbauer spectra of synthesized powders depends on the ratio between the characteristic times τ and τ_s . The superparamagnetic relaxation of monodomain particles can be determined with the help of the so-called blocking temperature T_B . This is a temperature, at which τ and τ_s becomes equal for a particle with definite averaged K and V values. The parameter T_B is considered as a certain limit, at which the transition from the superparamagnetic state into the magnetically ordered one takes place. It is described by the formula

$$T_B = \frac{KV}{k_B \ln \frac{\tau_s}{\tau_0}}. \quad (4)$$

At temperatures higher than T_B , the condition $\tau \ll \tau_s$ is satisfied, which gives rise to the appearance of a quadrupole doublet in the Mössbauer spectra. Below the blocking temperature ($\tau \gg \tau_s$), the Zeeman sextet is observed.

For a set of particles with a certain size distribution, experimental Mössbauer spectra, as a rule, look like a superposition of components with various relaxation times τ , because the parameter τ is very sensitive to the particle size (volume). Fluctuations of the average projection of the particle magnetic moment on a certain direction within the “time of observation” of the system give rise to the broadening of lines in the Mössbauer spectrum.

The integrated intensity of doublets superposed on the broadened magnetic sextuple in the Mössbauer spectra of ferrite powders increases with the substitution degree with Zn^{2+} cations. This fact can testify that the total volume of monodomain particles increases. For such particles, the individual value of T_B is lower than the measurement temperature, and, hence, they are in the supermagnetic state. In order to confirm the assumptions made above, the additional Mössbauer spectroscopy researches of synthesized powder were carried out at temperatures of 150 and 88 K. The Mössbauer spectra obtained for the Mg–Zn ferrite with $x = 0.5$ at temperatures of 300 and 150 K are shown in Fig. 4. The decrease of the measurement temperature brought about a reduction of the integrated intensity of the doublet component. Namely: its relative contribution amounted

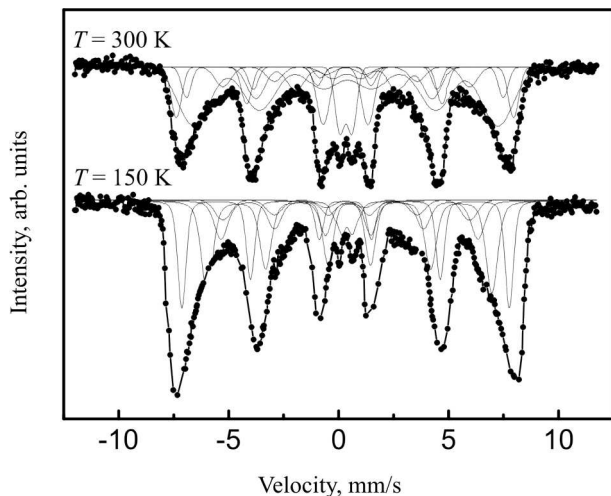


Fig. 4. Mössbauer spectra of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite registered at various temperatures

to 15.3% at room temperature, to 6.8% at a temperature of 150 K, and to 2.7% at 88 K. However, it should be noted that, in the latter case, the obtained value was smaller than the error of measurements.

The results of low-temperature research of synthesized powders testifies that the number of particles, for which T_B is lower than the measurement temperature, considerably changes at 150 K. Therefore, in the examined powders of magnesium-zinc ferrites, superparamagnetism arises for those nanoparticles, for which T_B is lower than the measurement temperature. According to some estimations [21, 22], the corresponding particle size should be equal to about 10 nm. We may assume that the relative fraction of those particles decreases with a reduction of the zinc cation concentration in the powders. This assumption agrees with the results of measurements of the specific surface area S in the synthesized specimens carried out by the method of adsorption porosimetry. As the concentration of zinc cations increases, the value of S monotonically grows from 1.2 to 4.6 m^2/g , which is evidently a consequence of a reduction in the linear dimensions of particles.

The superparamagnetic component of substituted powders was registered in the Mössbauer spectra in the form of two doublets with the isomeric shifts, δ , within the interval 0.28–0.47 mm/s and the quadrupole splittings, Δ , within the interval 0.51–1.24 mm/s determined by the symmetry of the nearest environment of the ^{57}Fe nucleus. The parameters

of the Mössbauer spectral components for the superparamagnetic phase of magnesium-zinc specimens are quoted in Table 2. The isomeric shift is known to diminish, if the 4s-electron density at ^{57}Fe nuclei grows. At the same time, the obtained δ -values testify to the presence of only trivalent iron cations in the specimens [23]. On the other hand, the quadrupole splitting values characterize the degree of deviation from the cubic symmetry of the spinel structure. It probably occurs because of a small particle size, so that crystallization is not complete, and any asymmetry in the nearest environment of Fe^{3+} cations results in nonzero values of quadrupole doublets. The results of work [24] confirm this conclusion: the quadrupole splittings for large-crystal Mg–Zn ferrites obtained at a temperature of 1100 °C fall within the interval 0.27–0.38 mm/s.

Concerning the magnetically ordered phase with the size of particles larger than 10 nm, it should be noted that an increase of the Zn^{2+} content in specimens results in a decrease of the effective magnetic fields at ^{57}Fe nuclei within the limits from 51 to 36 T. It is evident that a reduction of the magnetic fields weakens the A–B interaction in the spinel structure.

According to Néel's theory, the indirect superexchange A–B interaction in spinel ferrites dominates over the A–A and B–B interactions intrinsic for each of the sublattices. The indirect superexchange interaction between magnetic cations in the sublattices A and B of spinel ferrites is known to result in a magnetic ordering. In the magnesium-zinc ferrites, Zn^{2+} and Mg^{2+} cations are non-magnetic; therefore, they do not participate in the interaction. Hence, the magnetic ordering in the magnesium-zinc ferrites occurs owing to the superexchange A–B interaction between Fe^{3+} cations.

The substitution of Fe^{3+} cations by Zn^{2+} ones weakens the interaction, which is testified by the distribution of cations. Therefore, the effective magnetic field expectedly decreases with the growth of the zinc concentration. This conclusion is confirmed by the results of work [25], where the width of a ferromagnetic resonance line was found to decrease with the growth of the Zn^{2+} concentration in the specimens owing to a weakening of the antiferromagnetic interaction between the A and B sublattices.

The effective magnetic field also decreases with a reduction of the size of particles. For example, the

effective magnetic field H_{eff} equals 49 T for particles about 29 nm in dimensions in the case of a ferrite powder with $x = 0.2$, and $H_{\text{eff}} = 36$ T for $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ particles with an average size of 18 nm. The dependences of the effective field on the particle size is a result of oscillations of the magnetization vector around the direction close to the easy magnetization axis [26].

4. Conclusions

To summarize, magnesium ferrite powders with a certain content of doping zinc are obtained, by using the SGAC technology. The specimens had a spinel cubic structure of the spatial group $Fd\bar{3}m$. The average particle dimensions in the examined ferrites decrease with the growth of the Zn^{2+} cation concentration. The powder particles are found to agglomerate. The CSR size varied from 18 to 32 nm, whereas the average size of agglomerates did not exceed 100 nm. There is a pronounced correlation between the CSR size and the specific surface area in the examined powders. Zn^{2+} cations occupy sites only in the A sublattice and displace Fe^{3+} cations into the B sublattice, which weakens the superexchange A–B interaction. As the zinc content in the studied ferrite powders increases, the broadening of the lines in the Zeeman sextets, which arises at a chemical disorder, is observed. The Mössbauer spectra of specimens with non-magnetic substitution demonstrate doublets, which arise owing to the superparamagnetic relaxation. The latter took place because of the presence of single-domain nanoparticles with so small dimensions that their blocking temperatures are below the measurement (room) one. The intensity of doublets increases with the parameter x .

Hence, powders of magnesium-zinc ferrites synthesized with the help of the SGAC method contain nanoparticles that are in the supermagnetic state at the measurement temperature. Therefore, the presence of such particles was responsible for such a magnetic property as superparamagnetism. At the same time, irrespective of the substitution degree, the presence of a magnetically ordered phase in the blocked state is undoubtedly observed.

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СИНТЕЗ ТА МАГНІТНА
МІКРОСТРУКТУРА НАНОЧАСТИНОК МАГНІЄВИХ
ФЕРИТІВ, ЗАМІЩЕНИХ ЦИНКОМ

Резюме

Методом золь-гель за участі автогоріння синтезовано нанорозмірні магній-цинкові порошки. На основі рентгенівських досліджень встановлено фазовий склад немагнітно заміщених феритових систем. Виявлено, що отримані складні оксидні порошки агломеровані. Агломерати складаються з декількох наночастинок з середнім розміром 18–32 нм. За даними катіонного розподілу магній-цинкових феритів встановлено, що катіони Zn^{2+} займають позиції в тетрапідґратці, витісняючи при цьому катіони Fe^{3+} в октапідґратку.

Мессбауерівський спектр для порошку магнієвого фериту, знятий за кімнатної температури, показав присутність двох характерних зееманівських секстетів. Для заміщених немагнітними катіонами феритів спектри Мессбауера є суперпозицією декількох секстетів, на які накладаються дублети. Дослідження також показали, що вигляд зееманівських спектральних ліній залежить від розміру частинок, що свідчить про їх суперпарамагнітні властивості. Обговорено залежність мессбауерівських параметрів таких, як ізомерний зсув, квадрупольне розщеплення, ефективне магнітне поле від концентрації катіонів Zn^{2+} . Висловлено припущення, що зміна ефективного магнітного поля зі збільшенням вмісту цинку в магній-цинкових феритах пов'язана з тим, що заміщення катіонів Fe^{3+} катіонами Zn^{2+} послаблює непряму обмінну взаємодію між А та В підґратками феритів зі структурою шпінелі, яка, власне, призводить до їх магнітного впорядкування.