

UDC 546.72.76.46+543.429.3

DOI: 10.15587/1729-4061.2017.112271

MÖSSBAUER STUDIES OF SPINELLIDES OF $Mg(Fe_xCr_{2-x})O_4$ SYSTEM OBTAINED BY THE HYDROXIDE CO-PRECIPITATION METHOD

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Досліджено магнію ферит-хроміти системи $MgFe_{2-x}Cr_xO_4$, одержані методом сумісного осадження гідроксидів з водних розчинів відповідних хлоридів. Встановлено, що магнітопорядкована фаза наявна в зразках тільки при $x > 1,6$. Аналіз результатів мессбауерівських та X-променевих структурних досліджень показав відхилення реального ближнього оточення іона заліза від найбільш ймовірного. Іонів Fe^{2+} в даних зразках не виявлено

Ключові слова: мессбауерівська спектроскопія, магнію ферит-хроміти, шпінель, кристалічна структура, метод осадження

Исследованы феррит-хромиты магния системы $MgFe_{2-x}Cr_xO_4$, полученные методом совместного осаждения гидроксидов из водных растворов соответствующих хлоридов. Установлено, что магнитоупорядоченная фаза присутствует в образцах только при $x > 1,6$. Анализ результатов мессбауэровских и рентгеноструктурных исследований показал отклонение реального ближнего окружения иона железа от наиболее вероятного. Ионов Fe^{2+} в данных образцах не обнаружено

Ключевые слова: мессбауэровская спектроскопия, магния феррит-хромиты, шпинель, кристаллическая структура, метод осаждения

1. Introduction

For some decades, magnesium ferrite-chromites of the $Mg(Fe_xCr_{2-x})O_4$ spinel structure obtained by various procedures attract scientific and practical interest. The wide range of properties determine their use in production of electrodes [1-3], as catalysts [4, 5], adsorbents [6] of materials with high resistance and low losses in the long-wave part of SHF range [7], etc.

In the process of ferritizing, there is a possibility of saving free iron (III) oxide which promotes appearance of a significant quantity of Fe^{2+} during its transformation

to magnetite. To reduce dielectric losses in ferrite, it is necessary to hinder saving of free iron (III) oxide and formation of Fe^{2+} ions by improving batch homogeneity. High chemical homogeneity can be attained with the help of the method of co-precipitation of metallic hydroxides. However, the technologically controlled properties of the systems obtained by this method differ from the properties of ferrites synthesized by a conventional ceramic method.

That is why it is vital to establish regularities in magnetic characteristics of ferrite-spinels obtained by other than classical ceramic technology.

2. Analysis of the published data and problem statement

Paper [8] presents results of crystallographic studies and Raman spectroscopy of ferrite of $\text{MgCr}_x\text{Fe}_{2-x}\text{O}_4$ ($0 \leq x \leq 1$) system and works [9, 10] have revealed crystal-chemical and magnetic properties of the $\text{MgCr}_x\text{Fe}_{2-x}\text{O}_4$ system ferrites obtained by the ceramic technology from a mixture of oxides. Magnesium chromite with lattice parameter of 8.3347 Å and average particle size of 85–124 nm was synthesized from solutions of metallic nitrates in a stoichiometric ratio by hydrothermal method at various pH, temperature and time values [11]. Production of MgCr_2O_4 built in silicon dioxide matrix of nitrates of corresponding salts with the help of redox reaction with 1,3-propanediol was described in [12]. Electrical resistivity of nanoferrites of $\text{MgCr}_x\text{Fe}_{2-x}\text{O}_4$ ($0 \leq x \leq 1$) system obtained by gel-citrate method was measured by authors of work [13]. However, no data on studies of magnetic microstructure by Mössbauer spectroscopy were given in papers [8–13].

Mössbauer studies of magnesium ferrite-chromates of a general formula $\text{MgFe}_{2-x}\text{Cr}_x\text{O}_4$ ($x=0; 0.25; 0.5; 0.75; 1.0$) synthesized by the method of co-precipitation from nitrate salts with the use of NaOH were carried out in [14]. Spectra of samples with $x=0.25; 0.5$ are similar and demonstrate a symmetrical doublet. Because MgCr_2O_4 has normal structure and MgFe_2O_4 possesses partially inverse structure, a gradual transition of Fe^{3+} ions from octahedral to tetrahedral position will take place with increase in iron content. Spectrum of the sample with $x=0.75$ shows that Fe^{3+} ions start to occupy neighboring positions. Mössbauer spectrum of MgFe_2O_4 demonstrates magnetic ordering in a form of sextet with asymmetrical broadening of spectral lines superimposed on the doublet in the central part.

Mössbauer spectra of $\text{Fe}_{1-x}\text{Mg}_x\text{Cr}_2\text{O}_4$ spinellides up to $x=0.5$ exhibit only a singlet indicating that the substitution of cations in other coordination sphere does not contribute to anisotropy of the gradient of electric field on the nuclei of tetrahedral Fe^{2+} ions [15]. Mössbauer studies of MgFe_2O_4 synthesized by the ceramic technology showed absence of Fe^{2+} ions [16] while authors of work [17] reported formation of quite a large number of Fe^{2+} ions in samples of MgFeCrO_4 and $\text{MgFe}_{0.6}\text{Cr}_{1.4}\text{O}_4$. Besides, Mössbauer studies of the $\text{Mg}_{1-x}\text{Zn}_x\text{FeCrO}_4$ ($0 \leq x \leq 1$) samples produced by the ceramic technology were carried out in [18], and samples of $\text{Fe}_{1-x}\text{Mg}_x\text{Cr}_2\text{O}_4$ were studied in [19].

Because of presence of Cr^{3+} ions and non-magnetic Mg^{2+} ions, chromites of this system can have a frustrated magnetic structure, that is, a structure in which magnetic order does not extend to the entire volume of the sample but there are separately magnetized microscopic regions. The authors of [20] suggest that synthesized specimens may have clusters of the same type of ions which leads to appearance of regions enriched with iron and chromium atoms and a significant number of $\text{Fe}^{3+} - \text{Fe}^{2+}$ bonds in spinellides with a high magnesium content. A similar situation is described in [21].

It can be concluded from the analysis that the magnetic microstructure of magnesium ferrite-chromites significantly depends on the conditions of the sample synthesis and the available data are not unambiguous. At the same time, the literature does not contain data on magnetic microstructure and Mossbauer studies of samples having composition of $\text{Mg}(\text{Fe}_x\text{Cr}_{2-x})\text{O}_4$ obtained from chlorides of corresponding metals by the method of co-precipitation of hydroxides. Also,

the issue of presence of Fe^{2+} ions in spinels of this composition remains unresolved and contradictory.

3. The study objective and tasks

This study objective was to establish regularities in formation of magnetic microstructure of ferrite-spinels of $\text{Mg}(\text{Fe}_x\text{Cr}_{2-x})\text{O}_4$ composition obtained by co-precipitation of hydroxides from chlorides of corresponding salts. This will make it possible to determine micromagnetic parameters of the ferrites obtained by this method and provide new information for scientists and engineers working in the field of synthesis and use of ferrite materials in technology.

To achieve this goal, the following tasks were set:

- synthesize ferrite-spinels of $\text{Mg}(\text{Fe}_x\text{Cr}_{2-x})\text{O}_4$ composition by the method of co-precipitation of hydroxides from chlorides of corresponding salts and determine their basic crystallochemical parameters;
- establish regularities in the nature of the super-exchange interaction in the $\text{Mg}(\text{Fe}_x\text{Cr}_{2-x})\text{O}_4$ system with the use of Mössbauer spectroscopy;
- determine presence (or absence) of Fe^{2+} ions in spinels of $\text{Mg}(\text{Fe}_x\text{Cr}_{2-x})\text{O}_4$ composition synthesized by the method of co-precipitation of hydroxides from chlorides of the corresponding salts.

4. The results obtained in the study of magnesium ferrite-chromites synthesized by the method of hydroxide co-precipitation

4.1. Production of magnesium ferrite-chromites and structural studies

A series of magnesium ferrite-chromites with the general formula $\text{Mg}(\text{Fe}_x\text{Cr}_{2-x})\text{O}_4$ was synthesized for studying the method of co-precipitation of hydroxides. The initial components were aqueous solutions of chlorides: $\text{MgCl}_2 \times 6\text{H}_2\text{O}$, $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ and $\text{CrCl}_3 \times 6\text{H}_2\text{O}$. brand, concentrated ammonia solution, brand, chloric acid and distilled water. The content of magnesium, iron and chromium in aqueous solutions after separation of sediments in the process of ferrite synthesis was determined by complexometric titration. The washed and filtered precipitates were dried at 100–110 °C and sintered at 1000 °C for 4 hours followed by air hardening.

The phase-composition study of the sintered powders was carried out by X-ray diffraction analysis in $\text{Rh}_{\text{K}\alpha}$ radiation using ARL 9800 diffractometer and in $\text{Cu}_{\text{K}\alpha}$ radiation using the DRON-3 diffractometer (USSR).

The qualitative phase analysis of the samples showed that they are monophasic in the entire range of substitutions and correspond to the spinel lattice with the spatial $\text{Fd}\bar{3}\text{m}$ group. With the increase in the degree of substitution with iron x , displacement of peaks was observed on diffractograms of the sintered samples which is due to the growth of a constant lattice from 0.833 nm to 0.838 nm (Fig. 1, dot lines). This is explained by the entry of iron ions of a large ion radius in the crystal lattice due to substitution. In additions, Fig. 1 shows parameters of the lattice of synthesized samples calculated theoretically according to the Poi equation [22] (dashed lines) depending on Fe content. Line 2 reflects a change in the lattice parameter during substitution of iron

for chromium in the case of normal spinel, that is, magnesium remains in tetrahedral cavities, and line 3 corresponds to the substitution of iron for chromium with a simultaneous growing migration of magnesium from tetrahedral cavities to octahedral ones (inverse spinel). The resulting spinel occupies an intermediate position between the normal and the inverse spinels.

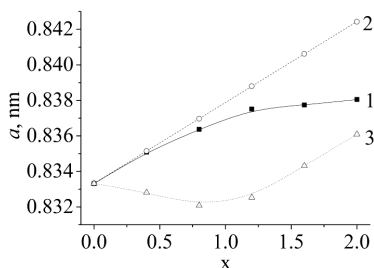


Fig. 1. Dependence of the a parameter of the $Mg(Fe_xCr_{2-x})O_4$ spinel elementary cell on the content of Fe (x): experimental values (1); theoretically calculated for normal and inverse spinels, respectively (2, 3)

Chromium ions tend to take octahedral positions, which relates to the structure of the electronic shell. All chromium spinels are normal, that is, they contain chrome only in the octahedral position. Ions Mg^{2+} and Fe^{3+} can take both tetrahedral and octahedral position, therefore, the $MgFe_2O_4$ spinel has a mixed type of cation distribution in sublattices [23, 24]. The studied magnesium ferrite-chromite system $Mg(Fe_xCr_{2-x})O_4$ can be written as $(Mg_{1-\epsilon}Fe_\epsilon)_A[Mg_\epsilon Fe_{x-\epsilon}Cr_{2-x}]_B O_4$ where ϵ is the Me^{3+} fraction in the tetrahedral sublattice, x is the number of Fe ions in the sample ($0 \leq x \leq 2$) and the cations located in the octahedral sublattice are taken in square brackets.

The cationic distribution of elements in sublattices was determined from experimental X-ray diffraction patterns using the FullProf program from the WinPLOTR software package in which a full-profile analysis was carried out by the Rietveld method.

An example of analysis of diffractograms of sintered ferrites of the marginal compositions $MgCr_2O_4$ and $MgFe_2O_4$ obtained with the use of copper radiation in the DRON-3 installation and the FullProf program is presented in Fig. 2 (experimental curves are plotted with red dots and theoretically calculated ones are plotted with solid black lines). Opposite the reflexes around the corner scale, there are blue vertical marks that correspond to the positions of the lines and Miller's indexes of the corresponding planes. As can be seen from Fig. 2, there is a good coincidence of intensities of experimental and theoretically calculated diffractograms throughout the angular range which indicates correctness of the determined crystallographic parameters. It is also worth paying attention to the significant difference in the ratios of the reflex intensities of the samples with marginal compositions: $MgCr_2O_4$ and $MgFe_2O_4$ (especially at small angles). Consideration of this difference in approximation of experimental diffractograms to theoretical ones is a confirmation of capability of obtaining correct dependencies of crystallochemical parameters on composition.

Dependencies of the cation distribution and crystallochemical parameters (the degree of ϵ inversion (the share of divalent cations in the octahedral position or trivalent

cations in the tetrahedral position), the anionic parameter U) of magnesium ferrite-chromites of the $Mg(Fe_xCr_{2-x})O_4$ system calculated by X-ray diffractometric data are presented in Fig. 3, 4.

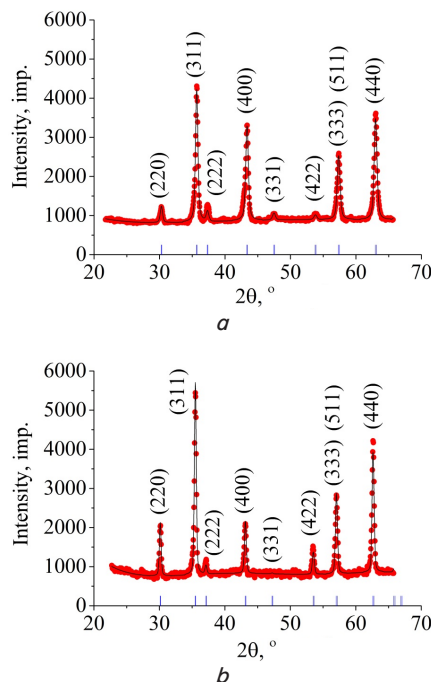


Fig. 2. Diffractograms of the ferrites with compositions: $a - MgCr_2O_4$; $b - MgFe_2O_4$ (red dots: experimental diffractograms, black lines: theoretically calculated diffractograms)

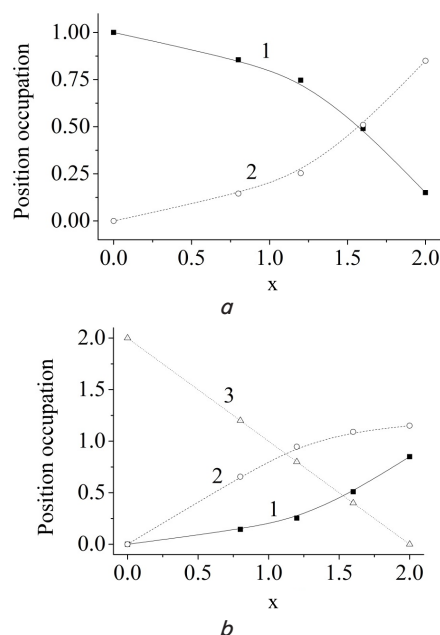


Fig. 3. Dependence of population of the $Mg(Fe_xCr_{2-x})O_4$ spinel sublattices Mg (1); Fe (2); Cr (3) on Fe (x) content: tetrahedral (a); octahedral (b)

As can be seen from Fig. 3, content of iron in both tetrahedral and octahedral positions increases with increase in iron quantity in the samples. At the same time, with high

content of iron, growth rate of its quantity increases in the tetrahedral sublattice, and decreases in the octahedral sublattice. Chromium content corresponds to that specified in synthesis of the composition and decreases linearly with the growth of substitution. Content of magnesium remains unchanged and is equal to 1, decreasing in tetrahedral and increasing in octahedral sublattice (at the same time, the rate of these changes increases with the growth of iron content in the samples). The anionic parameter which characterizes the degree of deviation from the ideal structure decreases with an increase in the content of iron in samples and the degree of ε inversion increases, too.

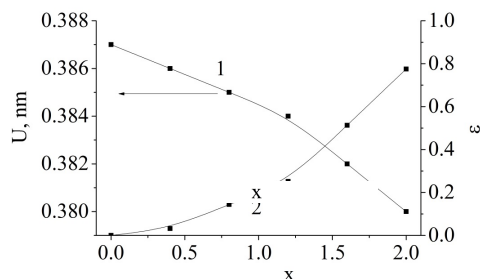


Fig. 4. Dependence of the anionic parameter $U(1)$ and the degree of ε inversion (2) of the $Mg(Fe_xCr_{2-x})O_4$ spinel on the Fe (x) content

4.2. Mössbauer studies of magnesium ferrite-chromites

To study magnetic microstructure of the samples, independent evaluation of quantitative values of iron distribution in sublattices and evaluation of presence of Fe^{2+} ions, Mössbauer studies were conducted.

Mössbauer spectra of absorption of magnesium ferrite-chromites were obtained at room temperature in an absorption geometry using a source of γ -quanta ^{57}Co with an activity of ≈ 100 mKu in a chromium matrix in a mode of constant accelerations in MS1104 Mössbauer spectrometer (Russia). The spectra obtained in order to find the parameters of its individual components were interpreted with the help of the universal MossWin Mössbauer program (Czech Republic).

Ferrites are complex magnetic systems, the nature of magnetic ordering in which is the result of competition of various types of over-exchange interactions. Presence of two sublattices that are non-equivalent in magnetic and crystallographic terms leads to a significant complication of the spectra. Correct interpretation is only possible with a sufficiently complete a priori information about the object of research in terms of crystallography. This information was obtained and analyzed in the previous paragraph.

In the first approximation, the resulting Mössbauer spectrum from spinel ferrites in which iron atoms are distributed between the tetra- and octanodes, is a superposition of two components. Analysis of the Mössbauer studies of such systems shows that the effective magnetic fields on the nuclei of octahedral Fe^{3+} cations have higher values than those of Fe^{3+} tetrahedral ions [25].

Magnesium ferrite-chromites with a spinel structure are typical non-compensated antiferromagnets. Formation of the magnetic moment in them occurs through an indirect over-exchange interaction via oxygen anions O^{2-} in the chains $(Fe^{3+})_A-O^{2-}(Fe^{3+})_B$ while magnetic moments of the tetra- and octapositions are oppositely directed.

Substitution of one ion for other leads to the necessity of accounting for the probabilities of a variety of the neighboring environment of the investigated Mössbauer nucleus [26]. Violation of the indirect exchange interaction during substitution of nonmagnetic ions for iron ions Fe^{3+} leads to appearance of magnet-nonequivalent positions of iron with less effective fields on Fe^{3+} nuclei. The spectra are not affected by the appearance of a paramagnetic doublet component with the number of magnetic neighbors ≤ 2 . For a correct analysis of experimental Mössbauer Fe^{57} spectra of the studied system of samples, the value of probability of formation of each of the nonequivalent positions of the Mössbauer Fe^{3+} atoms in octahedral position (Table 1) was calculated. The calculation was carried out according to the binomial distribution:

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

where z is a coordination number; n is the number of magnetic neighbors of Fe^{3+} ($0 \leq n \leq z$); k is the relative number of nonmagnetic neighbors.

Table 1

Distribution of the probability of formation of the magnet-nonequivalent positions of the Mössbauer spectra of Fe^{3+} atoms for octahedral position (values are given in percentages)

x	$P_0^{(0)}$	$P_1^{(1)}$	$P_2^{(2)}$	$P_3^{(3)}$	$P_4^{(4)}$	$P_5^{(5)}$	$P_6^{(6)}$
0.8	51	36	11	2	0	0	0
1.2	22	38	27	10	2	0	0
1.6	2	11	25	31	21	8	1

According to the Gileo model [27], magnetic cation having two or less magnetic exchange bonds with ions of other sublattice does not contribute to the total magnetization and behaves like a paramagnetic ion. Thus, there is a set of discrete values of local fields on the iron nuclei occupying several magneto-nonequivalent positions in octahedral positions. Therefore, according to Table 1, for samples with $x \leq 0.8$, the Mössbauer spectra with their components being only doublets are expected, for samples with $x=1.2$, spectra are expected with their components being intensive doublets ($\approx 80-90\%$) and sextiplets of insignificant intensity. In samples with $x > 1.6$, sextiplets of intensity and doublets of insignificant intensity should be observed.

Experimental Mössbauer spectra are shown in Fig. 5. Parameters of the Mössbauer spectra are presented in Table 2.

Table 2

Parameters of the Mössbauer spectra of magnesium ferrite-chromite

x	a, mm/s	I, mm/s	Q, mm/s	H_{eff} , kE	S, %
0.8	0.506 ± 0.01	0.448 ± 0.01	0.597 ± 0.01	–	100
1.2	0.546 ± 0.01	0.455 ± 0.01	0.608 ± 0.01	–	100
1.6	0.28 ± 0.02	0.34 ± 0.01	1.74 ± 0.03	365	2
	0.42 ± 0.01	0.57 ± 0.01	0.12 ± 0.01	–	98

Consequently, the spectra of samples with $x \leq 1.2$ consist of single doublets (Fig. 5, *a, b*). The values of isomer shifts and quadrupole splitting for samples with $x \leq 1.2$ correspond to iron ions in the trivalent state (Fe^{3+}). Absence of a magnetic superfine structure in the γ -resonance spectra indicates that Fe^{3+} ions which form the doublet component of the spectrum belong to the paramagnetic phase. This fact is due to the large number of nonmagnetic ions in the samples. However, in the spectrum of the sample with $x=1.2$, proceeding from the probability of formation of magneto-nonequivalent positions (Table 1), a sextiplet of slight intensity should also be observed. The absence of this sextiplet in the experimental spectrum shows the deviation of the real neighboring surrounding of the iron ion from the most probable environment. The reason for this is the method of making ferrites. The samples were obtained in a form of a fine powder which was sintered at $T=1000\text{ }^\circ\text{C}$ followed by air hardening. This led to reorientation of the magnetic moments of individual ions and their subsequent “freezing” in this state. It is necessary to note some thickening of the lines of doublets $a=0.506-0.546$ which is also due to hardening.

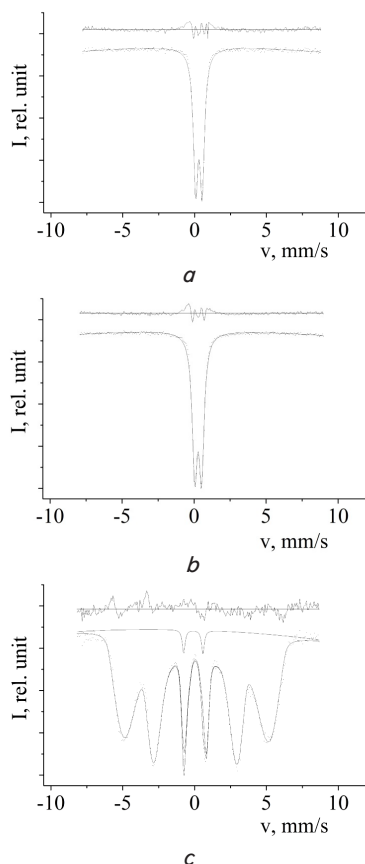


Fig. 5. Mössbauer spectra of magnesium ferrite-chromites:

- a* – $(Mg_{0,855}Fe_{0,145})_A[Mg_{0,145}Fe_{0,655}Cr_{1,2}]_B O_4$;
- b* – $(Mg_{0,747}Fe_{0,253})_A[Mg_{0,253}Fe_{0,947}Cr_{0,8}]_B O_4$;
- c* – $(Mg_{0,490}Fe_{0,510})_A[Mg_{0,510}Fe_{1,090}Cr_{0,4}]_B O_4$

The spectrum of the sample with $x=1.6$ (Fig. 5, *c*) consists of a paramagnetic doublet (2 %) and a relaxation sextiplet (98 %). The large magnitude of the quadrupole split indicates a low symmetry of the structure. In the spectrum, there is an intensive relaxation sextiplet although

according to Table 1 and the Gileo model, presence of an intense doublet is also expected. This is due to the fact that the temperature of sintering was not high enough for a complete relaxation of the magnetic superfine structure with transition to the paramagnetic phase. This led to the continual distribution of effective magnetic fields on the Fe^{3+} nuclei (Fig. 6). The most probable values of effective magnetic fields on Fe^{3+} nuclei are given in Table 3. In spinel, where there are only trivalent iron ions, effective magnetic fields on Fe^{57} nuclei and chemical shifts are larger for ions in octahedral nodes and smaller for ions in tetrahedral nodes. It can be concluded from Table 3 that Fe^{3+} ions with average values of $H_{eff3}=417\text{ kE}$ and $H_{eff2}=348\text{ kE}$ occupy octahedral and tetrahedral positions, respectively, while the magneto-nonequivalent position of Fe^{3+} ions with an average value of $H_{eff1}=229\text{ kE}$ is due to a nonmagnetic substitution and relaxation effects in the sample.

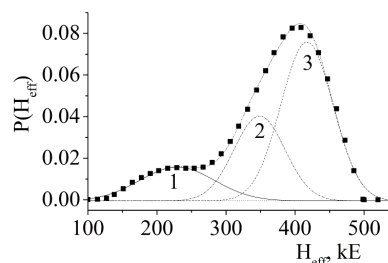


Fig. 6. Distribution of effective magnetic fields on Fe^{3+} nuclei in the sample $(Mg_{0,49}Fe_{0,51})_A[Mg_{0,51}Fe_{1,09}Cr_{0,4}]_B O_4$

Table 3

The most probable values of the effective magnetic fields on the Fe^{3+} nuclei in the sample $(Mg_{0,49}Fe_{0,51})_A[Mg_{0,51}Fe_{1,09}Cr_{0,4}]_B O_4$, $x=1.6$

No.	Effective magnetic field, kE	Integral intensity, %
1	229	16
2	348	29
3	417	55

Deviation of the near surrounding of iron ions from the most probable surrounding, as a result of sample hardening, causes appearance of local stressed clusters “frozen” from the synthesis temperature with a statistical ordering of cations in sublattices [28]. This indicates a mesoscopic model of structure of the studied isostructural solid solutions, that is, formation of a superposition of non-statistically ordered states.

5. Discussion of the results obtained in the study of formation of a crystalline and magnetic microstructure of the resulting spinellides

Advantages and disadvantages of using the method of hydroxide co-precipitation to obtain magnesium ferrite-chromites as well as a more detailed analysis of the crystallochemical parameters of these materials, was carried out by authors of this paper in [29].

The obtained spinel of the $Mg(Fe_xCr_{2-x})O_4$ composition occupies an intermediate position between normal and

inverse spinels. The anion parameter which characterizes the degree of deviation from the ideal structure decreases with an increase in the content of iron in the samples while the degree of inversion increases. Substitution of chromium for a part of trivalent iron ions in the spinel phases leads to normalization of the spinel structure.

As the amount of iron in the sample increases, the content of iron both in the tetrahedral and octahedral positions increases but at a high content of iron, the growth rate increases in the tetrahedral lattice while it decreases in the octahedral lattice. The content of chromium and magnesium corresponds to that specified during synthesis of the composition. The content of magnesium falls in the tetrahedral lattice and grows in the octahedral lattice (the speed of these changes increases with the increase in the content of iron in the samples).

At $x < 1.6$, the superfine magnetic structure is absent in the γ -resonance spectra which indicates that Fe^{3+} ions forming the paramagnetic component of the spectrum belong to the paramagnetic phase. Absence of sextiplets in the experimental spectra indicates the deviation of the real neighboring surrounding of the iron ion from the most probable surrounding. This is due to the method of making samples that were obtained in a form of a highly dispersed powder that was sintered at $T = 1000$ °C followed by air hardening.

At $x \geq 1.6$, sextiplets are observed in the γ -resonance spectra, that is, there is a magnetically ordered phase. Proceeding from the not high sample sintering temperature, low symmetry of the nearby surrounding and a continuous distribution of effective magnetic fields on the Fe^{3+} nuclei are observed.

The ratio of population of octahedral sublattice to that of the tetrahedral sublattice which was found from the data of X-ray diffraction analysis is 2.1 and a similar ratio calculated from the integral intensities of the Mössbauer sextiplets is 1.9. The obtained values (given the presence of relaxation sextiplet and the use of the model for continuous distribution of effective magnetic fields on the nuclei) can be considered well-coincidental. They confirm correctness of the results obtained in the analysis by both methods and the veracity of the conclusions drawn in the paper.

In the end, it should be noted that Fe^{2+} ions in the samples were not detected by the Mössbauer spectroscopy

method which is a good agreement with the literature data according to which Fe^{2+} ions are not formed if the chromium content is greater than 0.2.

The use of the co-precipitation method has made it possible to obtain single-phase magnetic magnesium ferrite-chromites at temperatures 300–500 °C lower than the typical ceramic technology. The obtained material, proceeding from the synthesis method, is characterized by high homogeneity of the chemical composition. It should be noted that the use of the co-precipitation method requires a detailed analysis of washing water to find the actual chemical composition of the material and minimize possible deviations from the expected chemical composition. The use of various types of cooling the material after its annealing (cooling in oven, hardening in air or in water) makes it possible to vary magnetic characteristics of the material within wide limits which creates a wide field for further scientific and technological studies.

6. Conclusions

1. Samples that are single-phase in the whole range of substitution, and have general formula $\text{Mg}(\text{Fe}_x\text{Cr}_{2-x})\text{O}_4$ ($0 \leq x \leq 2$) were synthesized by the method of co-precipitation of hydroxides from chlorides of the corresponding salts. The resulting spinel occupies an intermediate position between the normal and the inverse spinels. As the content of iron in the samples grows, the degree of inversion increases and the anionic parameter which characterizes the degree of deviation from the ideal structure decreases.

2. It was established that application of the method of co-precipitation of hydroxides from chlorides of the corresponding salts to obtain samples of $\text{Mg}(\text{Fe}_x\text{Cr}_{2-x})\text{O}_4$ ($0 \leq x \leq 2$) leads to formation of a paramagnetic material structure at $x < 1.6$. At $x \geq 1.6$, the relatively low sintering temperature (100 °C) leads to formation of a nearby low-symmetric cationic surrounding of the resonant Fe^{57} nuclei which determines the relaxation nature of the fixed Zeeman sextiplets.

3. Absence of Fe^{2+} ions in ferrite spinels with $\text{Mg}(\text{Fe}_x\text{Cr}_{2-x})\text{O}_4$ composition synthesized by co-precipitation of hydroxides from chlorides of the corresponding salts was confirmed.

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Досліджено комплексоутворюючі властивості волокнистого комплексу на основі поліакрилонітрилу по відношенню до іонів міді(II) в сумішах вода-1,4-діоксан. Визначено константи стійкості комплексів міді(II) з гідроксамовими групами полімеру, стехіометричний склад отриманих комплексів. Встановлено вплив сольватаційних параметрів комплексу на процес комплексоутворення

Ключові слова: модифіковане поліакрилонітрильне волокно, комплексоутворення, константи стійкості, розчинник вода-1,4-діоксан

Исследованы комплексообразующие свойства волокнистого комплекса на основе полиакрилонитрила по отношению к ионам меди(II) в смесях вода-1,4-диоксан. Определены константы устойчивости комплексов меди(II) с гидроксамовыми группами полимера, стехиометрический состав полученных комплексов. Установлено влияние сольватационных параметров комплекса на процесс комплексообразования

Ключевые слова: модифицированное полиакрилонитрильное волокно, комплексообразование, константы устойчивости, растворитель вода-1,4-диоксан

UDC 541.8

DOI: 10.15587/1729-4061.2017.110135

RESEARCH INTO COMPLEXING PROPERTIES OF POLYACRYLONITRILE COMPLEXITE IN THE MIXTURES OF WATER-DIOXANE

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1. Introduction

Complexing fibers (complexites) are widely used in practice [1]. These polymeric materials have good kinetic, sorption, technical-operational characteristics. It is easy to produce filters, tapes, non-woven materials out of them, which are suitable for hardware implementation of technological processes.

Complexites selectively sorb metal ions from solutions and form with them high-molecular complex compounds (HMCC) of various stability [2]. Due to these properties, HMCC are used in catalysis, ionometry, for sorption-spectroscopic and test methods of analysis of the solid phase of ion exchange materials, and analytical chromatography. Thus, when designing technological modes of wastewater purification from heavy metal ions with the help of complex-

ing fibers-complexites, it is necessary to establish in advance optimal variants for fixing metal ions with polymers.

Special features of complexing processes involving polymeric ligands of the crosslinked structures are related to their cooperative nature [3]. Cooperative nature of complexites manifests itself in various interactions of functional groups in the polymer chain, its configuration and supramolecular changes, determining the conformation of matrix of a polymer and groups. In other words, in such systems, the primary balance, a heterogeneous chemical reaction of formation of supramolecular complex compounds between polymer groups and metal ions, is accompanied by the above-mentioned so-called "polymeric effects" [3]. The latter influence physical-chemical characteristics of HMCC and are the reason why their properties differ from analogous properties of low molecular complex compounds (LMCC) [2].