

T.R. Tatarchuk, E.V. Boyko, I.P. Yaremiy, B.I. Rachiy, S.V. Fedorchenko

Synthesis, Crystal Chemistry and Antistructure Modelling of CoFe₂O₄ Nanoparticles Prepared by Citrate Sol-Gel Method

*Vasyl Stefanyk Precarpathian National University,
57, Shevchenko Str., Ivano-Frankivsk, 76018, Ukraine
Tel. (0342) 59-61-62; (050) 086.73.45, e-mail: tatar_ch@inbox.ru*

Cobalt ferrite nanoparticles were synthesized by the citrate sol-gel method and characterized by XRD, FT-IR, TG-DSC techniques. X-ray analysis confirms the formation of single phase cubic partially inverse spinel structure with the average particle size of 37 nm. Distribution of cations among the two interstitial sites (tetrahedral and octahedral sites) has been estimated by analyzing the powder X-ray diffraction pattern by employing Rietveld refinement technique. The FT-IR study between 4000 and 370 cm⁻¹ shows two absorption bands corresponding to tetrahedral and octahedral sites of CoFe₂O₄ spinel structure. Crystalloquasichemical model of formation CoO and Fe₂O₃ defects phases and their interactions was described.

Keywords: cobalt ferrite, spinel, sol-gel method, auto combustion, defect.

Стаття поступила до редакції 09.07.2014; прийнята до друку 15.09.2014.

Introduction

Among spinel ferrites, cobalt ferrite (CoFe₂O₄) has received special attention because of its large magneto-crystalline anisotropy, high coercivity, moderate saturation magnetization, large magneto-strictive coefficient, chemical stability and mechanical hardness [1]. CoFe₂O₄ is one of the most promising candidates for biologic applications, including magnetic resonance imaging (MRI), magnetic fluid hyperthermia (MFH), magnetic separations, biosensors, targeted and controlled drug delivery [2].

CoFe₂O₄ has an inverse spinel structure. The majority of spinel compounds belongs to space group Fd3m. The Bravais lattice of the conventional unit cell is face-centered cubic (FCC). There are 96 interstices between the anions in the cubic unit cell, however, in AB₂X₄ compounds, only 24 are occupied by cations. Of the 64 tetrahedral interstices that exist between anions, 8 are occupied by cations. The remaining 16 occupy half of the 32 octahedral interstices [3].

Properties of magnetic compounds depend on preparing method. There are a lot of preparing method including coprecipitation method [1, 4, 5], normal and reverse micelles methods [5], hydrothermal synthesis [6-7], sonochemical reactions [8] and sol-gel method [9-11]. Last one is the method of preparing metal oxide nanoparticles based on the transformation homogenous

sol to viscous gel with following burning. In this paper CoFe₂O₄ nanoparticles were prepared by citrate sol-gel method. It contains forming metal citrate complexes with next polymerization process which leads to forming viscous gel. This gel combusts and metal oxide powder is obtained. For describing possible types of defects crystalquasichemical method was used. It includes studying nature and concentration of defects depending on their location in the crystal.

I. Experimental

The chemicals used for the preparation of the samples were ferric nitrate (Fe(NO₃)₃·9H₂O, Mw=403,8597 g/mole), cobalt (II) nitrate (Co(NO₃)₂·6H₂O, Mw=290,943 g/mole), citric acid (C₆H₈O, Mw=192,06 g/mole) and ammonia solution (25%).

CoFe₂O₄ nanoparticles have been prepared by using citrate sol-gel method (Fig.1). Co(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O were dissolved in 200 ml distilled water under constant stirring to get homogeneous solution. Citric acid was dissolved in 100 ml distilled water and added to metal citrates solution in molar ratio of 1:1. Then the resulting solution was stirred at 20°C with addition ammonia solution to get pH = 7,0. After having been stirred, the sol was being heated at 100°C until the brown gel was formed. This gel combusted and fluffy product was obtained.

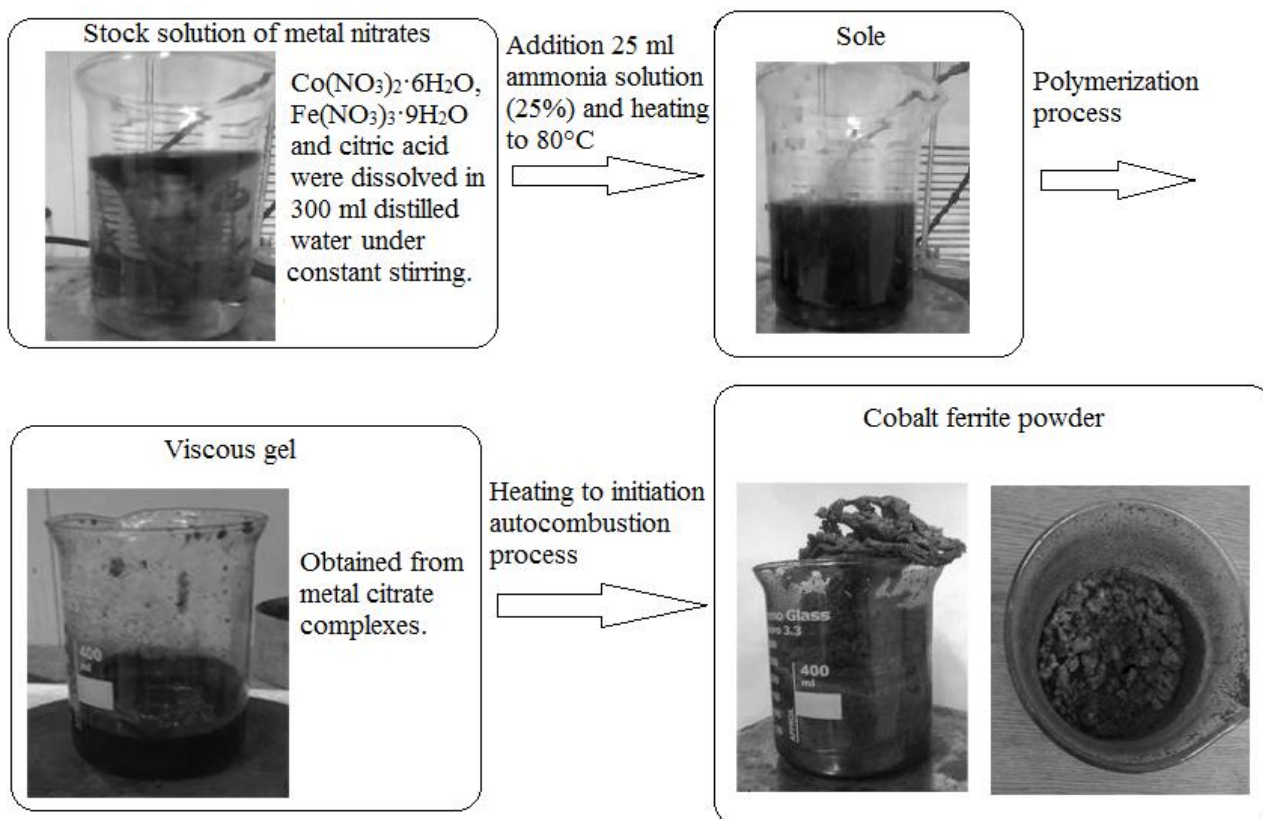


Fig. 1. The general flowchart of nanosized cobalt ferrite sample preparation.

X-ray diffraction (XRD) pattern of the as-synthesized sample was taken using X-ray diffractometer DRON-3 with $\text{Cu}_{K\alpha}$ radiation of wavelength $\lambda = 0,15406$ nm at 30 kV and 15 mA. The X-ray diffraction patterns were recorded in the angular range $15^\circ \leq 2\theta \leq 65^\circ$ with a step size of $0,05^\circ$. XRD pattern was analyzed by Rietveld method by the software FullProf.

Fourier transmission infrared (FT-IR) spectrum of the powders was recorded in the range $4000\text{--}370$ cm^{-1} by means of an Alpha-P Fourier-transform infrared spectrometer (Bruker) in ATR mode on diamond window with 256 scans at 6 cm^{-1} resolution. Each spectrum was the average of six ones.

The average crystallite size of CoFe_2O_4 nanoparticles was estimated using Scherrer's formula:

$$D_C = \frac{0,94\lambda}{\beta_{1/2} \cos \theta} \quad (1)$$

where D_C is the crystallite size, nm; $\beta_{1/2}$ – is the peak width at half-maximum intensity, degrees; θ is the Bragg angle, and λ is the wavelength of the X-ray radiation. To determine the crystallite sizes, the most three intense diffraction line (311), (511) and (440) were used.

The thermal behavior of powder precursor was characterized by Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA) by using simultaneous DSC/TGA analyzer NETZSCH STA 449F3 in order to analyze the mass loss and possible energy transitions. For the thermal analysis 35,366 mg of material was placed in Al_2O_3 crucible and heated up to 800°C at a rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ in argon.

II. Result and discussion

2.1. Thermogravimetric analysis.

The thermal decomposition of the metal-citrate precursor has been analyzed. The TG-DSC curves of the citrate precursor are shown in Fig. 2. From TG curve a weight loss of 10 % was observed over the temperature region $18\text{--}168^\circ\text{C}$ corresponding to desorption crystallization water. Weight loss of 74 % up to 203°C is observed from 168°C and small weight loss – above 203°C $\approx 5,81\%$ corresponding to decomposition metal-citrate precursor. The exothermic peak at the 214°C corresponds to the crystallization of the spinel phase of CoFe_2O_4 nanoparticles.

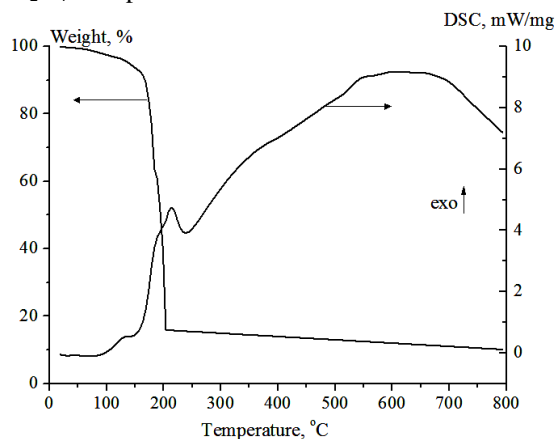


Fig. 2. Thermal curves (TG and DSC) for the metal-citrate precursor of CoFe_2O_4 .

2.2. X-ray diffraction analysis.

The phase identification and crystalline structure analysis were determined by the X-ray diffraction (Fig. 3). All the strong peaks appeared at $2\theta = 18,4^\circ, 30,2^\circ, 35,6^\circ, 43,3^\circ, 53,6^\circ, 57,2^\circ, 62,8^\circ$ are indexed to the crystal plane of spinel ferrite structure (111), (220), (311), (222), (400), (422), (551), (440) respectively. Characteristic diffraction peak of spinel cubic structure belonging to the $Fd3m$ space group. All reflection peaks were identified and indexed in good agreement with the referred database of the International Centre of Diffraction Data (ICDD).

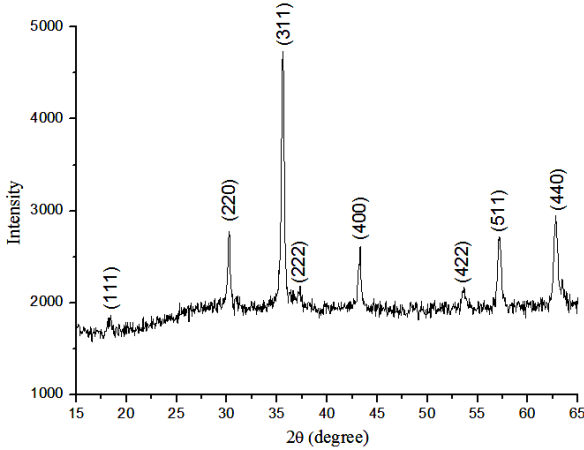


Fig. 3. Powder X-ray diffraction pattern of cobalt ferrite.

From XRD, crystallographic data were obtained. Thus, X-ray density (ρ_{XRD}), specific surface area (S), radius of the ions at octahedral site (r_{oct}), radius of the ions at tetrahedral site (r_{tet}) values were calculated for the next relationships [13]:

$$\rho_{XRD} = \frac{Z \cdot M}{N_A \cdot a^3} \quad (2)$$

$$r_{oct} = a \left(\frac{5}{8} - u \right) - R_O \quad (3)$$

$$r_{tet} = a\sqrt{3}(u - 0,25) - R_O \quad (4)$$

where M is molecular weight of the sample (g/mole), N_A is Avogadro's number ($6,023 \cdot 10^{23}$ atom/mole), Z – number of molecules per unit cell (for oxidic compounds with cubic spinel structure $Z=8$), a is lattice parameter obtained from XRD (nm), u – anion parameter (0,3749) and R_O – radius of oxygen ion (0,138 nm).

The specific surface area of the sample, S , was calculated using relationship [13]:

$$S = \frac{6000}{D_C \cdot \rho_{XRD}} \quad (5)$$

where D_C – crystallite size (nm), ρ_{XRD} – density calculated from XRD data (g/cm^3).

Crystallographic data for oxidic compound of $CoFe_2O_4$ are shown in Table 1.

Table 1

Crystallographic data for $CoFe_2O_4$

a_{exp} , nm	D_C , nm	ρ_{XRD} , g/cm^3	S , m^2/g	r_{oct} , nm	r_{tet} , nm
0,8377	37	5,304	30,57	0,0715	0,0432

Interionic distances were calculated from XRD data [3] and shown in Table 2.

Table 2

Spinel bond lengths as a function of anion parameter (u) and lattice parameter (a)

Species pair	Distance between lattice species	Value, nm
$Co_A^{2+} - O$	$\sqrt{3}a(u - 0,25)$	0,1812
$Co_A^{2+} - Co_A^{2+}$	$(\sqrt{3}/4)a$	0,3627
$Fe_B^{3+} - O$	$a(2(u - 3/8)^2 + (5/8 - u)^2)^{1/2}$	0,2053
$Fe_B^{3+} - Fe_B^{3+}$	$(\sqrt{2}/4)a$	0,2961
$Co_A^{2+} - Fe_B^{3+}$	$(\sqrt{11}/8)a$	0,3473

In spinel-type oxides the process of cation inversion is a very common phenomenon, being possible any distribution between a normal and an inverse spinel: $(A_{1-y}^{2+}B_y^{3+})_A [A_y^{2+}B_{2-y}^{3+}]_B (O_4^{2-})_O$ (A – divalent cations, B – trivalent cations, y – inversion parameter representing the fraction of A cations in octahedral sites). For obtained sample $y=0,8$ and cation distribution is described $(Co_{0,2}^{2+}Fe_{0,8}^{3+})_A [Co_{0,8}^{2+}Fe_{1,2}^{3+}]_B (O_4^{2-})_O$ (ICSD #39131).

During combustion and formation of $CoFe_2O_4$ particles, atom diffusion occurs in close proximity, followed by the rearrangement of metal cations. This could be explained by the quick combustion process, the energy released and the process duration being insufficient to ensure diffusion and migrations of atoms at large distances. The large volume of gas released at high speed during the combustion process restricts in the interactions between the constituents of the spinel lattice.

2.3. Fourier Transform Infrared Spectroscopy.

IR analysis is used to collect to obtain information about the structure of a compaund. Fig. 4 show the FT-IR absorption bands of $CoFe_2O_4$ produced by citrate method at room temperature in the wave number range of $4000-370\text{ cm}^{-1}$.

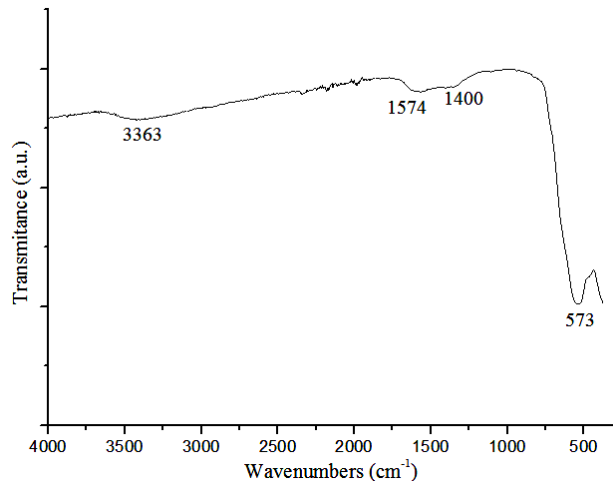


Fig. 4. FT-IR spectrum of the $CoFe_2O_4$.

Fig. 4 shows the presence of broad absorption bands at 537 cm⁻¹ assigned to the lattice vibrations corresponding to the Me³⁺-O²⁻ links from the tetrahedral positions (A). In the 400-350 cm⁻¹ wavenumber range, the adsorption bands noticed at low amplitude are attributed to the lattice vibrations of the corresponding Me²⁺ in octahedral positions (B). No characteristic band of nitrate ions at 1464 cm⁻¹ is observed from the FT-IR spectrum indicating the complete decomposition of nitrate precursors. Two peaks at 1574 and 1400 cm⁻¹ on the FT-IR spectrum are related to OH bond as reported in literature [12]. The band at 3363 cm⁻¹ is due to moisture (OH-groups).

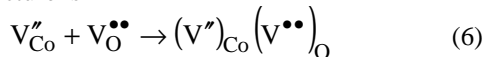
III. Crystalloquasichemical model of the formation spinel cobalt ferrite structure

Each chemical interaction is the result of atomic, ionic or molecular collisions which occur in gas and liquid systems. In solid state systems reaction zone is localized on the boundary of phase separation which is energetically heterogeneous and contains active centers initiating the reaction.

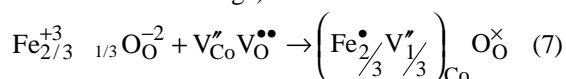
In this paper crystalloquasichemical model [14] the nature of defects and the mechanism of interaction between CoO and Fe₂O₃ oxide phases during the formation of cobalt ferrite spinel structure was described. Crystalloquasichemical mechanism provides superposition crystal structure with spinel antistructure V_A^{''}[V₂^{''}]_B(V₄^{''})_O, where • is an excess positive charge, '' and ''' is a double and triple excess negative charge respectively. The formation of different defect phases is possible depending on which oxide matrix or impurity is. Interaction of metal oxides on the matrix surface leads to form CoO | Fe₂O₃ sequence of layers. Processes on the surface CoO and Fe₂O₃ are treated separately with the formation of CoO and Fe₂O₃ defective phases, respectively.

3.1. Processes on the CoO surface.

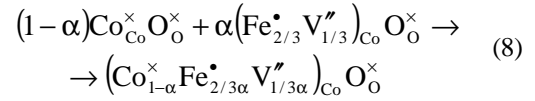
3.1.1. Stoichiometry for the anion. Matrix antistructure is the free vacancies that will remain if the cations and anions leave their positions. Quantity of vacancies is equivalent to quantity of cations and anions in matrix structure. If cation has positive charge then vacancy has negative charge. It means that vacancy is antiparticle of a certain ion. Similarly, for the anions. CoO antistructure is



where V_{Co}^{''} – cation vacancy, V_O^{''} – anion vacancy, (V'')_{Co}(V^{''})_O – matrix antistructure. The quantity of Oxygen in CoO and Fe₂O₃ must be equal in stoichiometry for the anion case. Therefore, we should take 1/3 mole of Fe₂O₃ or Fe_{2/3}³⁺ 1/3 O₂²⁻, where - is cation vacancy. Superposition matrix antistructure and impurity structure (× is an effective zero charge):

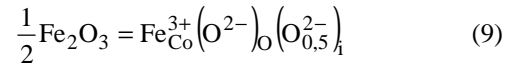


It has been obtained crystalloquasichemical cluster with defects type which is cation vacancies in result of interaction. For obtaining oxide with the same defects type we need to take α mole of the cluster and (1-α) mole of the matrix:

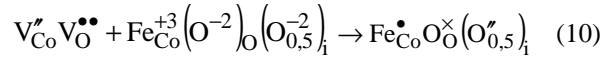


With the introduction of Fe₂O₃, Fe³⁺ ions occupy Co²⁺ units forming the Fe_{Co}[•] defects. In the result we obtained Co oxide with cation vacancies and electronic defects.

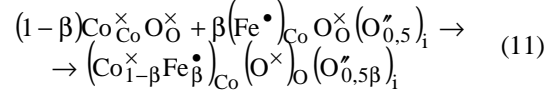
3.1.2. Stoichiometry for the cation. For the stoichiometry for the cation must be equal quantities of cations in certain oxides.



where (O_{0,5}²⁻)_i is rooted atom of Oxygen.



For obtaining 1 mole of oxide we need to take β mole of cluster and (1-β) mole of matrix:

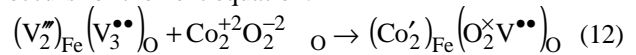


Obtained oxide is oxide with defect type of rooted atoms of Oxygen and electronic defects in Co sublattice.

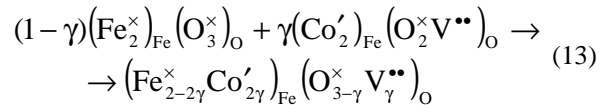
3.2. Processes on the Fe₂O₃ surface.

3.2.1. Stoichiometry for the cation. In this case we have a matrix – Fe₂O₃ and CoO is impurity. Matrix antistructure is (V₂^{''})_{Fe} (V₃^{''})_O.

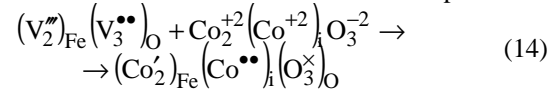
Stoichiometry for the cation CoO has the form of Co₂O₂. Superposition of matrix antistructure with Co₂O₂ occurs for the next equation:



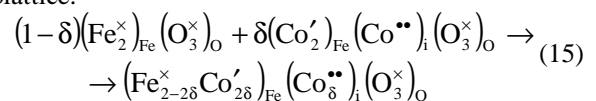
The interaction of γ mole of cluster and (1-γ) mole of matrix leads to form oxide with anion vacancies and Co atoms in Fe sublattice:



3.2.2. Stoichiometry for the anion. For obtaining a certain cluster stoichiometry for the anion Co₃O₃ interact with matrix antistructure for the next relationship:

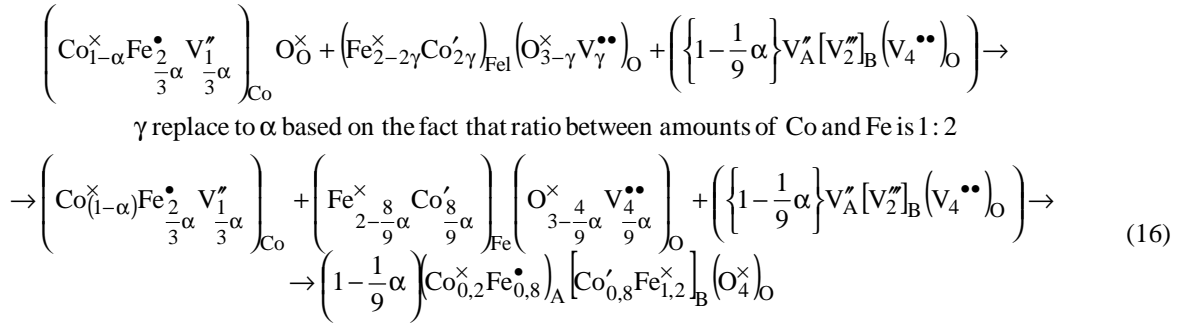


Result of interaction δ mole of cluster and (1-δ) mole of matrix is forming of oxide with defects type – rooted atoms of Cobalt and electronic defects in the iron sublattice:

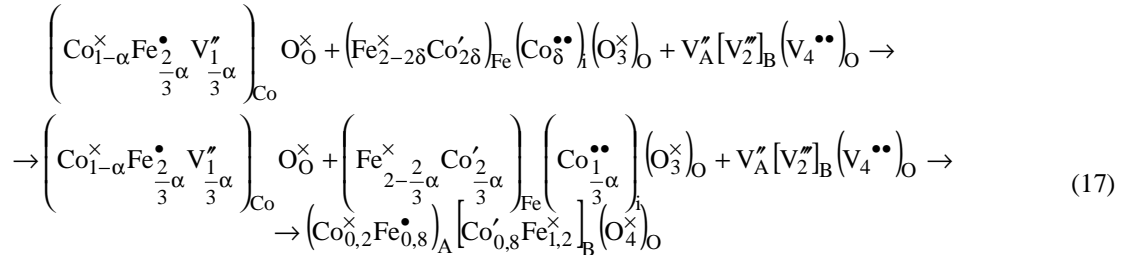


3.3. Formation of cobalt ferrite spinel structure.

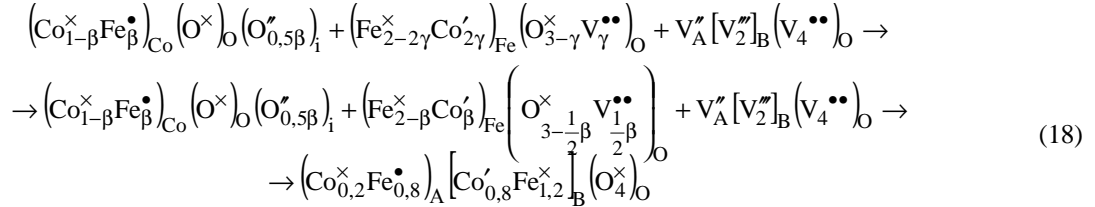
Obtained defect phases (8, 11, 13, 15) can interact between each other with forming spinel structure of cobalt ferrite. Clusters with cation vacancies interact with anion vacancies clusters.



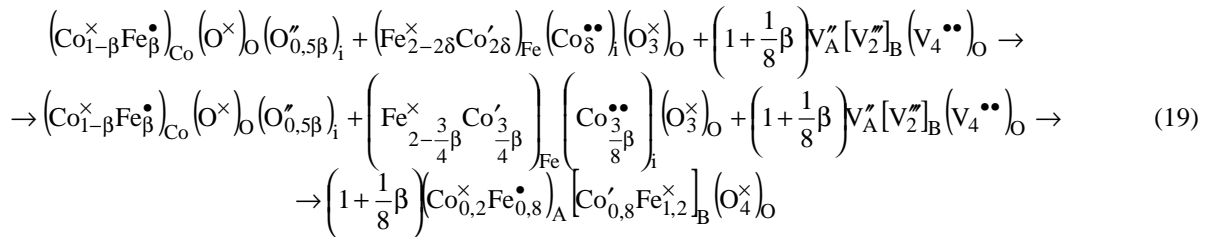
Interaction between (8) and (15) defect phases can be described



For next clusters we have



and for (11) and (15) clusters



Conclusions

In this paper, CoFe_2O_4 nanoparticles were synthesized by citrate sol-gel method. Addition of ammonia solution leads to formation NH_4NO_3 – auto combusting agent. The data obtained from XRD, FT-IR, DSC-TGA revealed that: the type of spinel is partially inverse – 0,2 mole of Co^{2+} occupy the tetrahedral (A) position, theoretical calculated crystallite size D being in the nanometer range. Also data corresponding to forming single phase cobalt ferrite without calcining product obtained from gel. This investigation indicates that this method of preparing spinel nanoparticles are useful and obtained products show good properties.

Acknowledgment

The authors are grateful to the professor Alexander Shyichuk (University of Technology and Life Sciences in Bydgoszcz, Poland) for the FT-IR spectrum and consultation in this study.

Татарчук Т.Р. – член-кореспондент Академії технологічних наук України, кандидат хімічних наук, доцент кафедри неорганічної і фізичної хімії ДВНЗ «Прикарпатський національний університет імені Василя Стефаника»;

Бойко Є.В. – студент Інституту природничих наук ДВНЗ «Прикарпатський національний університет імені Василя Стефаника»;

Яремій І.П. – доктор фізико-математичних наук, професор кафедри матеріалознавства і новітніх технологій ДВНЗ «Прикарпатський національний університет імені Василя Стефаника»;

Рачій Б.І. – кандидат фізико-математичних наук, старший науковий співробітник кафедри матеріалознавства і новітніх технологій ДВНЗ «Прикарпатський національний університет імені Василя Стефаника»;

Федорченко С.В. – кандидат технічних наук, доцент кафедри органічної та аналітичної хімії ДВНЗ «Прикарпатський національний університет імені Василя Стефаника».

- [1] Y. Kim, D. Kim, C. S. Lee, Physica B, 337, 42 (2003).
- [2] E. Alveroglu, H. Sozeri, U. Kurtan, M. Senel, A. Baykal, Journal of Molecular Structure, 1036, 386 (2013).
- [3] K. E. Sickafus, J. M. Wills, J. Am. Ceram. Soc., 82 (12), 3279 (1999).
- [4] V. V. Paike, P. S. Niphadkar, V. V. Bokade, P. N. Joshi, J. Am. Ceram. Soc., 90, 3009 (2007).
- [5] I. Sharifi, H. Shokrollahi, M. M. Doroodmand, R. Safi, Journal of Magnetism and Magnetic Materials, 324, 1854 (2012).
- [6] P. C. Morais, V. K. Garg, A. C. Oliveira, L. P. Silva, R. B. Azevedo, A. M. L. Silva, E. C. D. Lima, J. Magn. Magn. Mater., 225 (4), 37 (2001).
- [7] A. Cabanas, M. Poliakoff, J. Mater. Chem., 11 (5), 1408 (2001).
- [8] K. V. P. M. Shafi, A. Gedanken, R. Prozorov, J. Balogh, Chem. Mater., 10 (11), 3445 (1998).
- [9] Y. Hao, O. Lai, J. Lu, H. Wang, Y. Chen, X. Ji, Journal of Power Sources, 158 (2), 1358 (2006).
- [10] R. Thirunakarana, A. Sivashanmugama, S. Gopukumara, C. Dunnillb, D. Gregoryb, Materials Research Bulletin, 43 (8-9), 2119 (2008).
- [11] Z. Han, L. Dong, D. Zhang, Z. Wu, X. Zhang, Rare Metals, 25 (6), 462 (2006).
- [12] M. Aliahmas, M Noori, Indian J. Phys., 87, 431 (2013).
- [13] A.M. Dumitrescu, P.M. Samoila, V. Nica, F. Doroftei, A.R. Iordan, M.N. Palamaru, Powder Technology 243, 9 (2013).
- [14] S.S. Lisnyak, Neorganicheskie materialyi, 28 (9), 1913 (1992).

Т.Р. Татарчук, Є.В. Бойко, І.П. Яремій, Б.І. Рачій, С.В. Федорченко

Синтез, кристалохімія та антиструктурне моделювання наночастинок CoFe₂O₄, синтезованих цитратним золь-гель методом

*Прикарпатський національний університет імені Василя Стефаника,
вул. Шевченка, 57, м. Івано-Франківськ, 76018, Україна
Tel. (0342) 59-61-62; (050) 086.73.45, e-mail: tatar_ch@inbox.ru*

Наночастинки фериту кобальту синтезовано цитратним золь-гель методом та охарактеризовано за допомогою X-променевого аналізу, ІЧ-спектроскопії та диференціального термічного аналізу. X-проміневий аналіз підтвердив утворення однофазної кубічної частково оберненої шпінельної структури із середнім розміром частинок 37 нм. Розподіл катіонів між двома позиціями (тетраедричними і октаедричними) оцінено шляхом аналізу порошкових дифрактограм зразка з використанням методу Рітвельда. ІЧ-спектроскопічні дослідження в діапазоні 4000–370 см⁻¹ демонструють два абсорбційні піки поглинання, що відповідають тетраедричним та октаедричним позиціям шпінельної структури CoFe₂O₄. Описано кристалоквазіхімічну модель утворення дефектних фаз оксидів CoO та Fe₂O₃, взаємодія між якими призводить до утворення кобальтового фериту.

Ключові слова: кобальт ферит, шпінель, золь-гель, автогоріння, дефект.