

Preparation and investigation of nanodimensional nickel ferrite

Z. P. Cherkezova-Zheleva^{1*}, K. L. Zaharieva¹, V. S. Petkova²,
B. N. Kunev¹, I. G. Mitov¹

¹ Institute of Catalysis, Bulgarian Academy of Sciences, "Acad. G. Bonchev" St., Bl. 11, 1113 Sofia, Bulgaria

² Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Acad. G. Bonchev St.,
Block 107, 1113 Sofia, Bulgaria

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Nickel ferrites with different Ni content – $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$, $0 \leq x \leq 1$ are technologically important materials for microwave, electronic and magnetic storage devices. These materials are members of solid solution series of spinel-type materials (Fe_3O_4 – NiFe_2O_4) having specific magnetic properties and different degree of electron delocalization. They demonstrate good gas sensing properties and catalytic activity in various catalytic processes, such as complete oxidation of waste gases, oxidative dehydrogenation of hydrocarbons, decomposition of alcohols etc. Up today, much attention has been paid to the preparation of such nanocrystalline materials, because of difficulty of their synthesis procedures and special techniques used. However the problem is still topical. The nickel contained ferrite materials $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ($x=0.25, 0.5, 1$) were prepared by co-precipitation method using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ as precursors in our previous investigations. But small quantities of intermediate phase – FeOOH was obtained in synthesized material. So the aim of the study is to find cheap and easy way for preparation of nano-sized magnetite-type materials. In order to prepare single phase spinel material thermogravimetric, differential thermogravimetric and differential thermal analysis (TG, DTG and DTA), as well as different chemical and structural studies such as X-ray diffraction (XRD), Moessbauer spectroscopy, were done. As a result of investigation the appropriate preparation conditions are obtained. The synthesis procedure includes combination of co-precipitation combined with low temperature thermal treatment of materials.

Key words: nickel ferrites, nano-sized powders, low temperature treatment, thermal analysis, Moessbauer spectroscopy, X-ray diffraction analysis.

INTRODUCTION

Preparation of high-quality magnetic nanoparticles with a narrow size distribution, reproducible physical properties and production with short processing times is one of the key issues in nanoparticle research today. Recent studies have also focused on the development of novel synthesis techniques for the production of uniform magnetic oxide materials [1]. Nanoparticles with controlled sizes and properties can be synthesized by wet chemical techniques [2]. It is known that the crystal size is related to the relative interdependence between the nucleation and growth steps, which in turn can strongly be affected by the solution chemistry and precipitation conditions [3].

Nanosized NiFe_2O_4 is one type of ferrite that has been studied intensively. It shows peculiar structural and magnetic properties. Small particle size promotes a mixed spinel structure whereas the bulk form is an inverse spinel. As far as the magnetic properties of these materials are concerned, spin glass like behavior can be considered as the most interesting property that leads to high field irreversibility, shift of the hysteresis loops, and anomalous relaxation dynamics [4]. The properties of ferrite particles are influenced by the composition and microstructure, which are sensitive to the preparation methodology used in their synthesis [5]. The magnetic and the electrical properties of ferrites are reported to be highly sensitive to the cation distribution, which in turn depend on the material of synthesis and sintering conditions [1]. The catalytic properties of spinels containing transition metal ions are dependent on the redox properties of substituting ions and on their distribution among the octahedral and tetrahedral coordination sites. The surface of

* To whom all correspondence should be sent:
E-mail: zzhel@ic.bas.bg

spinel oxide powders contains mainly octahedral sites and, consequently, its catalytic activity is crucially related to the octahedral cations [6].

The main direction of our present research is to obtain a single phase nano-sized nickel ferrites $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ($x=0.25, 0.5, 1$) promising as catalyst and magnetic material. In order to obtain this ferrite material will be made low temperature treatment at different temperatures of nickel contained ferrite sample produced by chemical co-precipitation procedure. The structural properties of samples at each stage of the synthesis are studied using the following methods as Thermal analysis, X-ray diffraction analysis, Moessbauer spectroscopy.

EXPERIMENTAL

The nickel contained ferrite samples: *Sample A* – $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ($x=0.25$), *Sample B* – $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ($x=0.5$) and *Sample C* – $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ($x=1$) were produced using chemical co-precipitation method described in details previously [7]. Dried brown ferrite powders were investigated by using several methods for characterization.

The thermal analysis as TG, DTG and DTA are obtained with a “Stanton Redcroft” (England) installation equipped with a PC. The 10.00 mg prepared nickel contained ferrite samples are heating in the temperature range 20–1000 °C at 10 °C/min heating rate in stabilized corundum crucible and air medium with flow – 1l/h.

Moessbauer measurements were carried out with apparatus Wissenschaftliche Elektronik GmbH, working with a constant acceleration mode, $^{57}\text{Co}/\text{Cr}$ source, $\alpha\text{-Fe}$ standard. The computer fitting was used to determine the parameters of hyperfine interactions of Moessbauer spectral components: isomer shift (IS), quadrupole splitting (QS), hyperfine effective magnetic field in the site of iron nuclei (H_{eff}), line widths (FW) and component relative weights (G).

X-ray diffraction (XRD) patterns of the nanostructured nickel ferrite samples during the synthesis were performed with a TUR M62 apparatus with computer management and data collection, working with HZG-4 goniometer and $\text{CoK}\alpha$ radiation. The presence of the phases was determined with JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997). Scherrer equation was used to made calculation of the average crystallite size, lattice microstrain parameter and unit cell parameter of the ferrite samples [8].

The effect of thermal treatment of the nickel contained ferrites is investigated for different times and at different temperatures in argon medium in the furnace “Eurotherm”, England.

RESULTS AND DISCUSSION

Series of nickel contained ferrite samples with different stoichiometry $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ($x=0.25, 0.5$ and 1) were produced using co-precipitation procedure [7]. These materials are members of solid solution series of spinel materials $\text{Fe}_3\text{O}_4\text{-NiFe}_2\text{O}_4$ and different degree of incorporation of Ni metal ion in the magnetite host matrix is expected. Physicochemical characterization of materials shows their ultradisperse character. However small quantities of intermediate oxihydroxide phase (FeOOH) was also obtained in

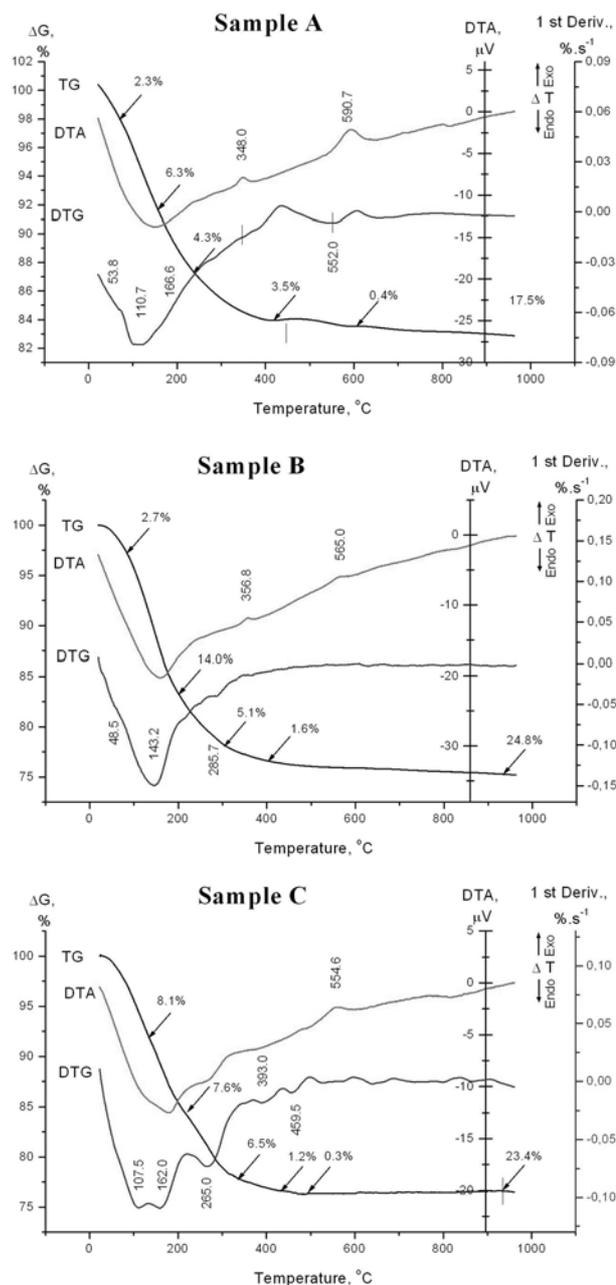


Fig. 1. TG, DTG and DTA curves of synthesized nickel contained ferrite samples

all samples, due to incompletely realized synthesis process. In order to prepare single phase material number of initial analysis are carried out. The behaviour of synthesized ferrite materials during the thermal treatment gives results concerning the further investigations about effect of calcinations as the dehydration and dehydrogenation temperatures and crystallisation processes (see Fig. 1).

Moessbauer spectra of the studied samples after thermal treatment are presented on Figure 2. In all three cases the spectra represent superposition of sextet-type lines only. The spectra are fitted by the CONFIT program using several models for the fitting procedures. The best spectra fit show the presence of two or three sextuplet components in all registered spectra. The calculated Moessbauer parameters are shown in Table 1. The obtained hyperfine parameter values of these components show presence of tetrahedrally coordinated Fe^{3+} ions in a spinel phase – Sxt1 and octahedrally coordinated Fe^{3+} ions in a spinel phase – Sxt2. The calculated hyperfine parameter values of the third sextet component (Sxt 3) show the presence of octahedrally coordinated iron ions in third oxidation degree, which are included in the $\alpha\text{-Fe}_2\text{O}_3$ (Hematite) phase [9]. With an increase of Ni content, the relative weight of hematite phase decreases and in the case of *Sample C* only octahedrally and tetrahedrally coordinated iron ions in spinel structure are detected [10].

Figure 3 shows the XRD patterns of nickel contained ferrite materials after thermal analysis. The formation of the non-stoichiometric spinel ferrite phase $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ (PDF-10-0325; 75-0449) and different amount of hematite $\alpha\text{-Fe}_2\text{O}_3$ phase (PDF-73-2234) are observed in the *Sample A* – $\text{Ni}_{0.25}\text{Fe}_{2.75}\text{O}_4$ and *Sample B* – $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$ respectively. Diffraction peaks due to single phase cubic spinel ferrite NiFe_2O_4 (PDF-10-0325) are indexed in the *Sample C* – NiFe_2O_4 . The sharp and broad lines in the three XRD patterns indicate the presence of highly dispersed particles and high crystallinity of the synthesized ferrite materials. The average particle size, lattice microstrain parameter and unit cell parameter of studied spinel phase was calculated by

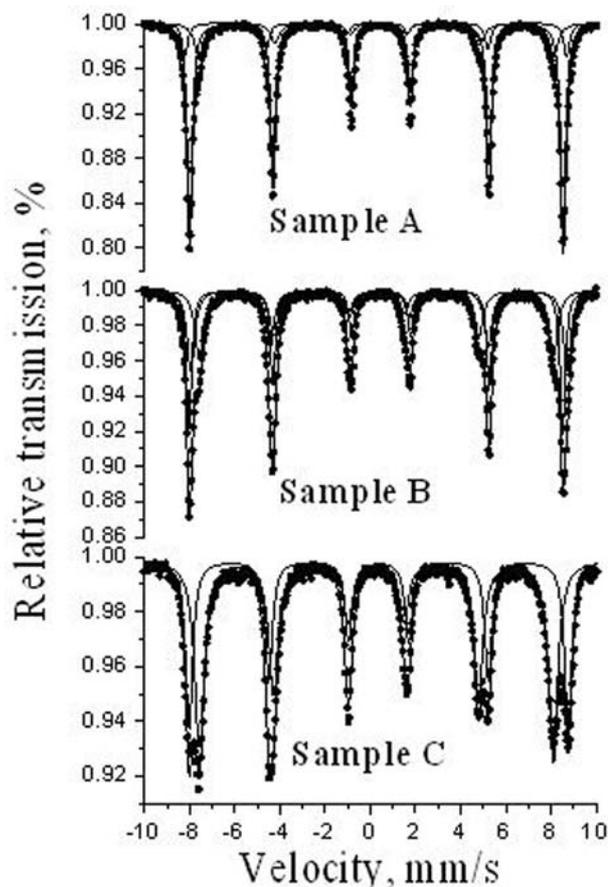


Fig. 2. Moessbauer spectra of synthesized nickel contained ferrite materials after thermal analysis

Scherrer equation [8]. The obtained values can be seen in Table 2. It can be seen that the mean crystallite size of spinel ferrite particles is about 20–35 nm. The obtained results for the presented phases and their relative weights in studied samples are in very good agreement with Moessbauer data.

On the base of the obtained results, thermal behavior of investigated materials is resolved. Three stages of weight loss in the TG curves are established (Fig. 1). The main mass losses – 8.6%, 15.7%

Table 1. Moessbauer parameters of samples after DTA

Sample	Components	IS, mm/s	QS, mm/s	$H_{\text{eff}}^{\text{Fe}}$, T	FMHW, mm/s	G, %
Sample A – after DTA	Sxt 1 – $\text{Fe}^{3+}_{\text{tetra}}$	0.34	–0.03	48.2	0.47	20
	Sxt 2 – $\text{Fe}^{3+}_{\text{octa}}$	0.20	–0.02	51.6	0.32	17
	Sxt 3 – Hematite Fe^{3+}	0.37	–0.20	51.4	0.28	63
Sample B – after DTA	Sxt 1 – $\text{Fe}^{3+}_{\text{tetra}}$	0.37	–0.01	48.5	0.41	35
	Sxt 2 – $\text{Fe}^{3+}_{\text{octa}}$	0.26	–0.01	51.8	0.47	33
	Sxt 3 – Hematite Fe^{3+}	0.37	–0.19	51.3	0.28	32
Sample C – after DTA	Sxt 1 – $\text{Fe}^{3+}_{\text{tetra}}$	0.37	0	48.7	0.37	49
	Sxt 2 – $\text{Fe}^{3+}_{\text{octa}}$	0.25	0.01	52.2	0.43	51

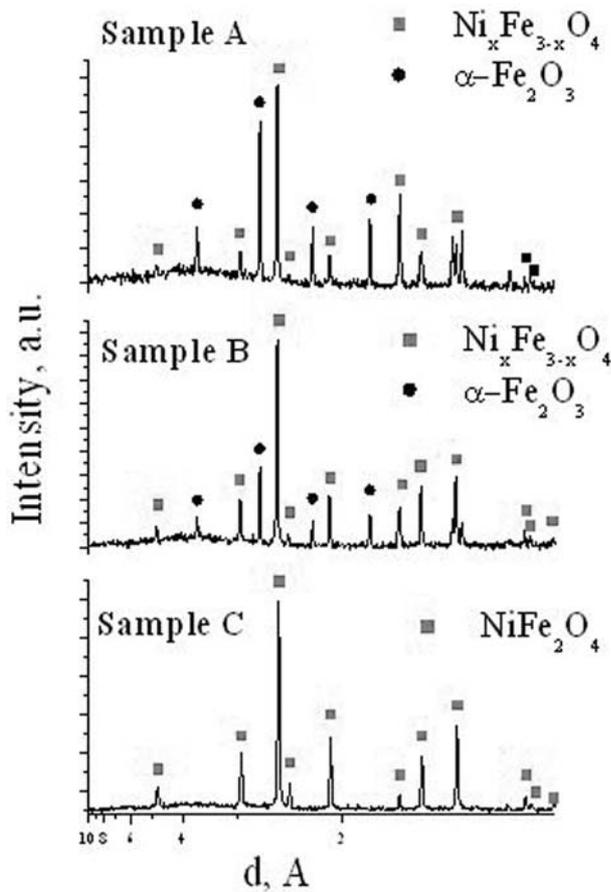


Fig. 3. XRD patterns of synthesized nickel contained ferrite materials after thermal analysis

and 16.7% results from dehydration process. The presence of endothermic peak in the temperature region 20–200 °C is related to remove of water molecules coordinated in crystal lattice. The exothermic effects at 348.0°C, 356.8°C of the ferrite materials *Sample A* – $\text{Ni}_{0.25}\text{Fe}_{2.75}\text{O}_4$ and *Sample B* – $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$ in the DTA curves and weight losses 7.8%, 5.1% and 6.5% are assigned to the thermal transformation of intermediate phase $\beta\text{-FeOOH}$ and formation of hematite phase $\alpha\text{-Fe}_2\text{O}_3$ respectively [11–14]. A high presence of hematite due to a low content of nickel in spinel ferrite $\text{Ni}_{0.25}\text{Fe}_{2.75}\text{O}_4$ explains the more intensive exothermic peak at 348.0 °C com-

pared with this one at 356.8 °C for $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$. The absence of exothermic effect around this temperature in the thermal behavior of ferrite material *Sample C* – NiFe_2O_4 is connected with the presence of single spinel ferrite phase only. The registered DTA thermograms of all studied samples show the second exothermic peak at 590.7 °C, 565.0 °C and 554.6 °C, respectively. It can be attributed to formation and crystallization of nickel ferrite phase in all prepared ferrite samples.

In order to prepare single phase materials the co-precipitated samples have to be heated in inert atmosphere to avoid oxidation. The interpretation of the above presented thermal analysis data gives as a result the appropriate temperature of heating 300 °C. The crystal water from the materials is dehydrated at temperatures lower than 300 °C and therefore the synthesis of ferrites below this temperature can be done. The lowest temperature to start the synthesis in isothermal conditions is 300 °C. A fresh reaction surface is formed, during the process of dehydration. Getting a fresh reactive surface and the heating in the inert atmosphere, are a basics for the synthesis of ferrite compounds. Figure 4 presents the X-ray diffraction pattern of *Sample B* – $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$

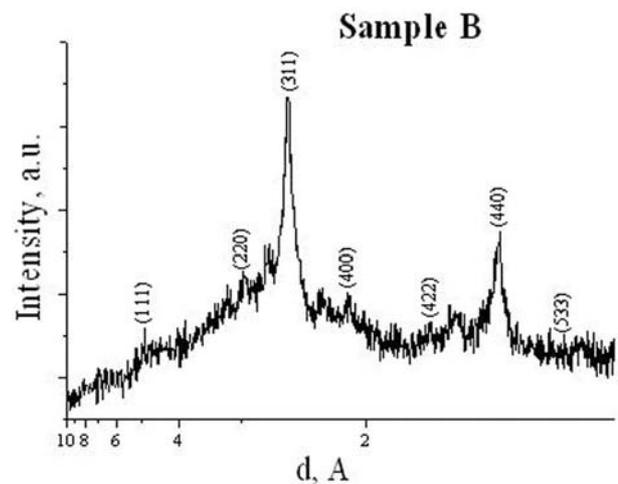


Fig. 4. XRD pattern of *Sample B* – $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$ after heating at 300 °C in argon media

Table 2. Calculated values of mean crystallite size (D), lattice strain (e) and unite cell parameter (a) of spinel ferrite phase

Sample	D, nm	e, a.u	a, Å
$\text{Ni}_{0.25}\text{Fe}_{2.75}\text{O}_4$	21	$3,5 \cdot 10^{-3}$	8.34
$\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$	28	$2,4 \cdot 10^{-3}$	8.33
NiFe_2O_4	34	$0,7 \cdot 10^{-3}$	8.31

after heating at 300 °C in inert atmosphere (Ar media) as an example. It clearly shows the preparation of ultra dispersed single phase spinel material. The exact composition of sample will be established by chemical analysis, but all studied materials are members of solid solution series Fe_3O_4 (PDF-75-0449) – NiFe_2O_4 (PDF-10-0325). The presence of single phase composition shows the incorporation of Ni^{2+} ions in the magnetite host matrix.

CONCLUSIONS

Physicochemical characterization of prepared by co-precipitation procedure series of ferrite materials with different stoichiometry $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0.25, 0.5, 1$) are carried out using different techniques. The DTA-TG study and the obtained analysis results show the dehydration and dehydrogenation temperatures and crystallisation processes, as well as the appropriate conditions for preparation of single phase materials. High dispersion and nano-size particles is registered in all studied samples. The studied materials are members of solid solution series of magnetite-type materials (Fe_3O_4). With increasing of Ni-content in materials increasing of particle size is obtained. The low temperature thermal treatment at 300 °C in argon media leads to production of single phase spinel nickel ferrite material.

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СИНТЕЗ И ИЗСЛЕДВАНЕ НА НАНОРАЗМЕРЕН НИКЕЛОВ ФЕРИТ

З. П. Черкезова-Желева^{1*}, К. Л. Захариева¹, В. Петкова²,
Б. Н. Кунев¹, И. Г. Митов¹

¹ *Институт по катализ, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 11, 1113 София, България*

² *Институт по минералогия и кристалография, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 107, 1113 София, България*

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(Резюме)

Никеловите ферити с различно съдържание на никел – $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$, $0 \leq x \leq 1$ са технологично важни материали за микровълнови, електронни и магнитни запомнящи устройства. Тези материали са представители на серия от твърди разтвори на шпинелов тип материали ($\text{Fe}_3\text{O}_4\text{--NiFe}_2\text{O}_4$), имащи специфични магнитни свойства и различна степен на електронна делокализация. Те показват добри газ-детекторни свойства и висока каталитична активност в различни процеси като пълно окисление на отпадъчни газове и летливи органични съединения, окислително дехидрогениране на въглеводороди, разлагане на алкохоли и др. Понастоящем голямо внимание се отделя на получаването на такива нанокристални материали. Проблемът все е още актуален поради редица трудности при техния синтез и използването на специални техники. Никел-съдържащи феритни материали $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ($x=0.25, 0.5, 1$) са получени по метода на утаяване с използване на $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ и $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ като прекурсори в наши предишни изследвания. Но в синтезираните материали са регистрирани малки количества междинна фаза – FeOОН . Цел на изследването е да се намери евтин и лесен начин за получаването на наноразмерни материали от магнетитов тип. С цел да се получат еднофазни шпинелни материали са проведени термогравиметричен, диференциален термогравиметричен и диференциален термичен анализ, както и различни химични и структурни изследвания като рентгенова дифракция и Мьосбауерова спектроскопия. В резултат на изследването са намерени подходящите условия на получаване. Синтезът включва процес на утаяване, комбинирано с ниско температурна термична обработка на материалите.