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The synthesis and characterization of nickel and cobalt ferrite nanopowders obtained by different methods

I. Zalite, G. Heidemane, L. Kuznetsova, M. Kodols, J. Grabis
Institute of Inorganic Chemistry of the Riga Technical University,
P. Valdena iela 3/7, Riga, LV-1048, Latvia
E-mail: ilmars.zalite@rtu.lv

M. Maiorov
Institute of Physics of University of Latvia, Miera iela 32, Salaspils, LV-2169, Latvia

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The ferrite materials, especially of nickel and cobalt, are popular due to their unique mechanical and magnetic properties. The single phase $NiFe_2O_4$ and $CoFe_2O_4$ ferrites were synthesized by three methods: the high frequency plasma chemical synthesis, the sol-gel self-combustion, and the co-precipitation technology combined with the hydrothermal synthesis method. Magnetic properties, crystallite size, the specific surface area of synthesized products are characterized. Nanopowders synthesized in the high frequency plasma have a specific surface area in the range of 28–30 m^2/g (the average particle size 38–40 nm, crystallite size ~40 nm), but a wider particle size distribution is in the range of 10–100 nm with some particles of 200 nm. The ferrite nanopowders obtained by the sol-gel self-combustion and hydrothermal synthesis method have the specific surface area of 40 ± 3 and 60 ± 5 m^2/g (average particle size 25–30 nm and 19–26 nm, crystallite size 10–20 nm and 12–20 nm), respectively. Cobalt ferrites after synthesis are characterized by the saturation magnetization M_S of 75 emu/g (for plasma chemical synthesis), 53 emu/g (for the self-combustion method), and 57 emu/g (hydrothermal synthesis). The saturation magnetization for nickel ferrites is 44, 29 and 30 emu/g, respectively. After the thermal treatment up to 900 ºC the particle size of all ferrites increases, but their magnetic properties are approaching those of monolithic ferrites.

Key words: $NiFe_2O_4$, $CoFe_2O_4$, nanoparticles, synthesis, properties.

Introduction

Ferrites are a wide range of minerals and synthetic materials, which have been used in different fields of interests for a long time. The most significant and popular usage of ferrites are in optics, electronics, mechanics and other technical fields [1]. Ferrites are also of great importance in medicine, for biomedical purposes and in chemical catalysis. More information appears about hyperthermia in scientific articles. With this method, ferrite nanoparticles are introduced into a living organism, in controlled conditions nanoparticles are transported to the cancer zones in the organism, and in a magnetic field with thermal treatment the cancer cells are eliminated [2].

The properties of nanomaterials depend on their morphology, particle size and microstructure, so it is important to analyze the obtaining conditions and the method of synthesis of nanoparticles. Ferrites with a spinel structure are significant materials in the development of several technological applications where materials with a high density and a low porosity are necessary [3]. Ferrites, as most of the ceramic materials, are obtained in solid phase reactions from different oxides. By improving nanotechnology, several liquid phase and gas phase synthesis have been developed, such as hydrolysis, hydrothermal synthesis [4], pyrolysis, microwave synthesis [1], using the methods of co-precipitation [5], the sol-gel method [6], combustion [7] and plasma synthesis [8].

The aim of this research was to obtain nickel and cobalt ferrite nanopowders by three different methods and to compare their characteristics, including magnetic properties.

Experimental

In this research, the nickel and cobalt ferrite nanopowders prepared by the chemical sol-gel self-combustion (combust.) method, by co-precipitation technology, combined with the hydrothermal synthesis (hydrotherm.) method and by the high frequency plasma chemical synthesis (plasma), and their mechanical and magnetic properties have been studied.

For the production of ferrites by the high frequency (HF) plasma chemical synthesis, the technological equipment developed in the Institute of Inorganic Chemistry of the Riga Technical University was used [8]. Commercial metal and metal oxide (Ni, Co, NiO, CoO, and FeO) powders were evaporated in HF plasma to obtain ferrites. All powders in stoichiometric ratio (for the resulting products $NiFe_2O_4$ and $CoFe_2O_4$) have been introduced in the N_2 plasma with the average temperature of 5800–6200 K. After the powders evaporate, the vapours are very fast cooled with the cooling gas (air), and the product condensates on a filter, resulting in nanosized ferrite particles.

By the sol-gel self-combustion method cobalt and nickel ferrites were synthesized using reagent-grade

chemicals: $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3) \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, glycine, nitric acid [9]. 100 mL 0.1 M cobalt (or nickel) nitrate solution was added to 200 mL 0.1 M iron nitrate solution. Glycine and nitric acid were separately dissolved in 100 mL of distilled water, and both were added to the nitrate mixture. Glycine (Gly) was used as the self-combustion agent with the molar ratio Me/Gly = 1 : 0.8 and Gly/Nitr. = 1 : 4. The mixture was digested on a hotplate and mixed evenly with a mechanical overhead stirrer up to the moment when the mixture was congealed. The mixture was heated until igniting, and the heating continued for 4 h at 300 °C.

By the hydrothermal method, cobalt and nickel ferrites were synthesized using reagent grade chemicals: $FeCl_3 \cdot 6H_2O$, urea, $Co(NO_3)_2 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$, NaOH. The precursor was used in the hydrothermal synthesis: urea was hydrolyzed for 3 hours in the $FeCl_3$ solution (molar ratio 3 : 1) at 70–75 °C. Cobalt (or nickel) nitrate was added to the cooled reaction mixture. The molar ratio $FeCl_3 \cdot 6H_2O$: $Co(NO_3)_2 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ was corresponding to the stoichiometry of the metal ions in ferrite. The suspension was stirred continuously with the 40 % solution of NaOH, cobalt (or nickel) hydroxide was slowly precipitated until the *pH* of suspension was of 9–10, then inserted in the ultrasound bath for 20 min. and finally treated for 24 h at 40 °C. Then the precipitate is washed decanting with distilled water until the presence of Cl^- ion is not registered, and then treated hydrothermally in the optimum synthesis conditions (t = 250 °C, τ = 3 h, p = 17–17.5 MPa) [10].

All samples were analyzed by the X-ray diffractometer Advance 8 (Bruker AXS). The crystallite size was calculated by the Scherer's equation. The morphology and particle size of the powder particles were investigated by a transmission electron microscope JEM-100S (JEOL). Magnetic properties were analyzed by vibrating sample magnetometry (VSM Lake Shore Cryotronics, Inc., model 7404 VSM). The specific surface area (*SSA*) was measured with the BET single point method. Measurements were made at the boiling point of liquid nitrogen (–196 °C), and the adsorbing gas was Ar (~7 % Ar gas mixture in the He gas).

Results and discussion

The characteristics of synthesized ferrites are given in Table 1 and in Figs. 1–3. All of them were nanocrystalline stoichiometric single-phase powders (Fig. 1) with the specific surface area in a wide scope of 30–60 m^2/g depending on the method of synthesis, and the calculated particle size was 20–40 nm (Table 1). The crystallite size of ferrites was also in the scope of 10–40 nm. The finest particles were obtained by the hydrothermal synthesis, whereas powders obtained by the plasma synthesis had the widest distribution of particle size in the scope of 20–100 nm, with some particles up to 200 nm (Fig. 2). Nanopowders obtained by plasma synthesis have spheric particles.

None of the XRD patterns of samples obtained at the optimal synthesis conditions shows other additional phases (commonly magnetite, maghemite, hematite or other metal oxides), which proves that they are of high purity. When analyzing XRD patterns, there are slight differences between the relative intensities and the width of reflexes, if ferrite samples are compared depending on the synthesis method, and this indicates differences of the crystallite size. The self-combustion and hydrothermal synthesis method gives nanopowders with a smaller crystallite size than these obtained by the plasma synthesis (Table 1). The magnetic properties of ferrite nanopowders obtained by all methods are shown in Fig. 3. The magnetic properties (Table 1, Fig. 3) of nanopowders obtained by the plasma synthesis are very close to those of the standard bulk material (the magnetic saturation values are 80 emu/g for $CoFe_2O_4$ and 50 emu/g for $NiFe_2O_4$ [11]). This proves the high purity of the samples. However, the magnetic properties of samples obtained by the self-combustion and hydrothermal methods differ from those obtained by the plasma synthesis. Probably, it is due to the difference in the particle size of the nanopowders obtained by the plasma synthesis and the self-combustion and hydrothermal methods.

Table 1. Properties of synthesized ferrite nanopowders

Sample	*SSA*, m^2/g	d_{50}, nm*	Crystallite size, nm	Phase composition	Saturation magnetization M_S, emu/g	Remanent magnetization M_r, emu/g	Coercivity H_c, Oe
$CoFe_2O_4$ (plasma)	29	39	40 ± 5	$CoFe_2O_4$	75.4	32.0	780
$CoFe_2O_4$ (combust.)	37	31	20 ± 3	$CoFe_2O_4$	53.4	20.3	1170
$CoFe_2O_4$ (hydrotherm.)	61	19	12 ± 3	$CoFe_2O_4$	57.3	17.3	575
$NiFe_2O_4$ (plasma)	29	38	40 ± 5	$NiFe_2O_4$	44.2	10.0	74
$NiFe_2O_4$ (combust.)	43	26	10 ± 3	$NiFe_2O_4$	29.0	6.0	140
$NiFe_2O_4$ (hydrotherm.)	42	26	20 ± 3	$NiFe_2O_4$	39.0	2.6	23

* Average particle size calculated from SSA.

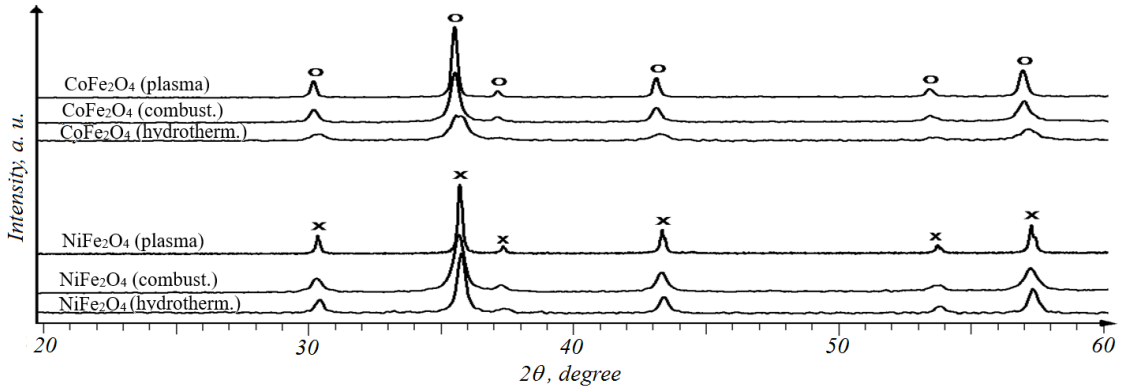

Fig. 1. XRD pattern of ferrite nanopowders: o – $CoFe_2O_4$, x – $NiFe_2O_4$.

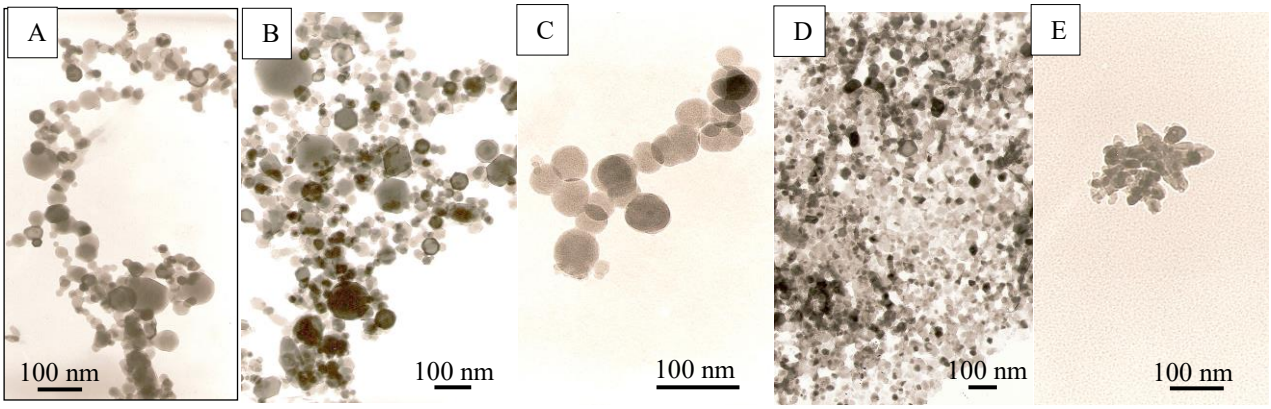

Fig. 2. The electron microscope image of $CoFe_2O_4$ (A, C) and $NiFe_2O_4$ (B, D, E) obtained by the plasma synthesis (A, B), self-combustion (C, D) and hydrothermal (E) methods.

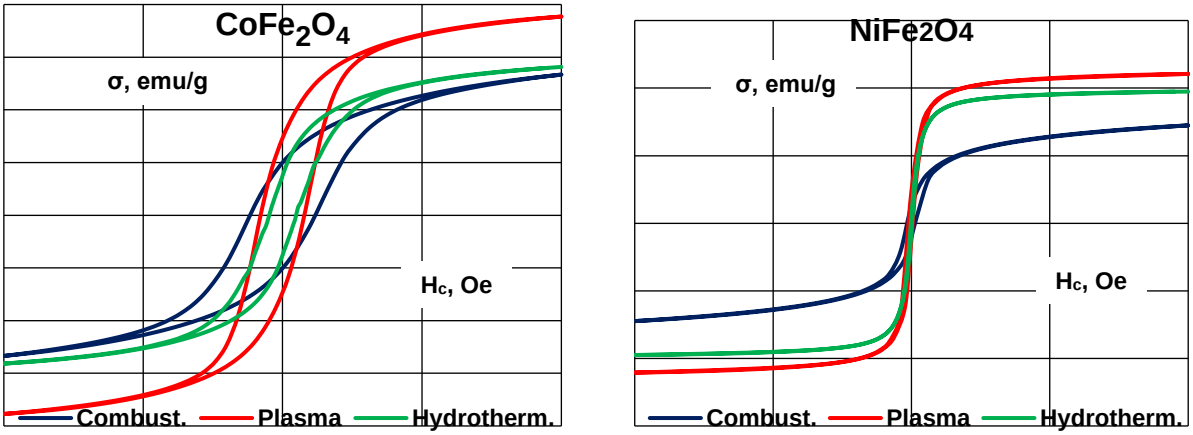

Fig. 3. Magnetic properties of ferrites synthesized by the sol-gel self-combustion and the hydrothermal method and in plasma.

Another interesting feature regarding nanopowders synthesized in the framework of this research is their magnetic behavior, i. e., although all of the synthesized powders have particle size below the critical single-domain limit (ca. 70 nm [12, 13]), the quasi-supermagnetic behavior is observed only in the case of plasma-synthesized $NiFe_2O_4$ nanoparticles.

After thermal treatment at higher temperatures, the specific surface area (SSA) of the ferrites synthesized by the self-combustion and hydrothermal method has a tendency to decrease, while the crystallite size increases. This tendency could be explained by the fact that particles are re-crystallizing and growing at higher temperatures, so the specific surface area is decreasing (Fig. 4). With increasing the temperature of thermal treatment, also the saturation magnetization of ferrites increases (Table 2, Fig. 5). For example, after thermal treatment at 800 ºC and more the magnetic saturation increased to 80 and 72 emu/g for $CoFe_2O_4$ produced via self-combustion and by the hydrothermal method, which is close to the values of the standard bulk material (80 emu/g for $CoFe_2O_4$ [12]).

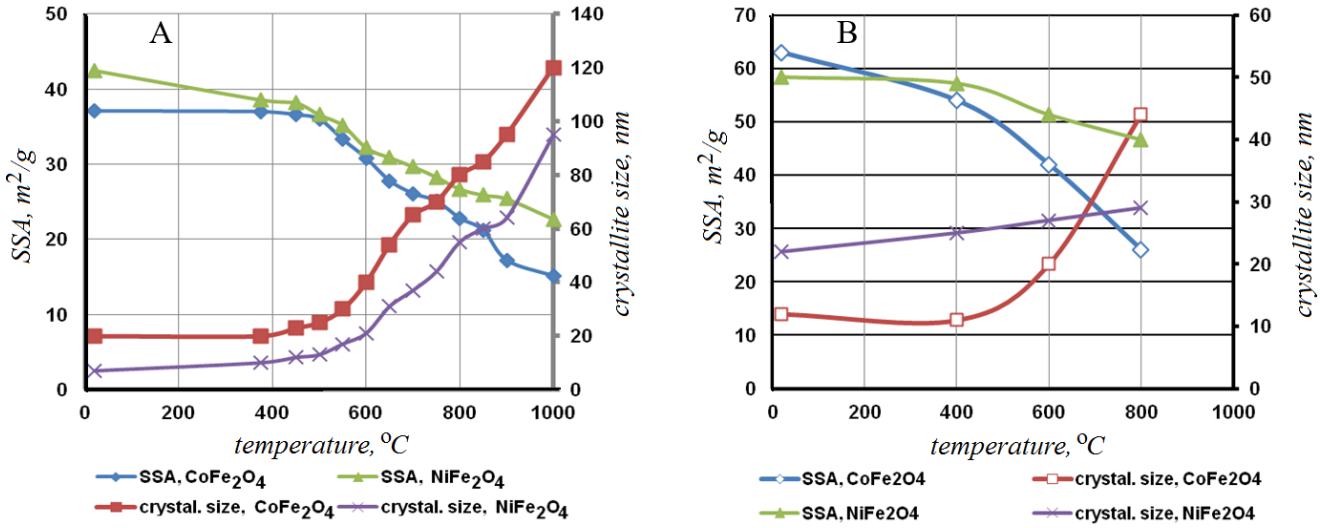

Fig. 4. Specific surface area (SSA) and crystallite size comparison depending on temperature for $NiFe_2O_4$ and $CoFe_2O_4$ synthesized by the sol-gel self-combustion (A) and the hydrothermal (B) method.

Table 2. Magnetic properties of ferrites synthesized by the sol-gel self-combustion and the hydrothermal method after thermal treatment (2 h at different temperatures)

Samples	Heating temperature, °C	Saturation magnetization M_S, emu/g	Remanent magnetization M_r, emu/g	Coercivity H_c, Oe
$CoFe_2O_4$ combust.	raw powder	53.4	20.3	1170
	450	55.0	21.7	1190
	650	76.1	39.3	1350
	850	79.9	35.7	930
	900	79.8	31.3	980
$NiFe_2O_4$ combust.	raw powder	29.0	6.0	120
	450	31.4	4.8	130
	650	37.4	9.1	200
	850	45.2	14.8	145
	900	47.4	15.0	135
$CoFe_2O_4$ hydrotherm.	raw powder	50.0	10.2	495
	400	50.1	12.6	390
	600	62.8	22.4	760
	800	71.6	28.9	875
$NiFe_2O_4$ hydrotherm.	raw powder	37.4	2.6	23
	400	36.7	3.8	34
	600	40.2	5.2	55
	800	42.6	5.0	70

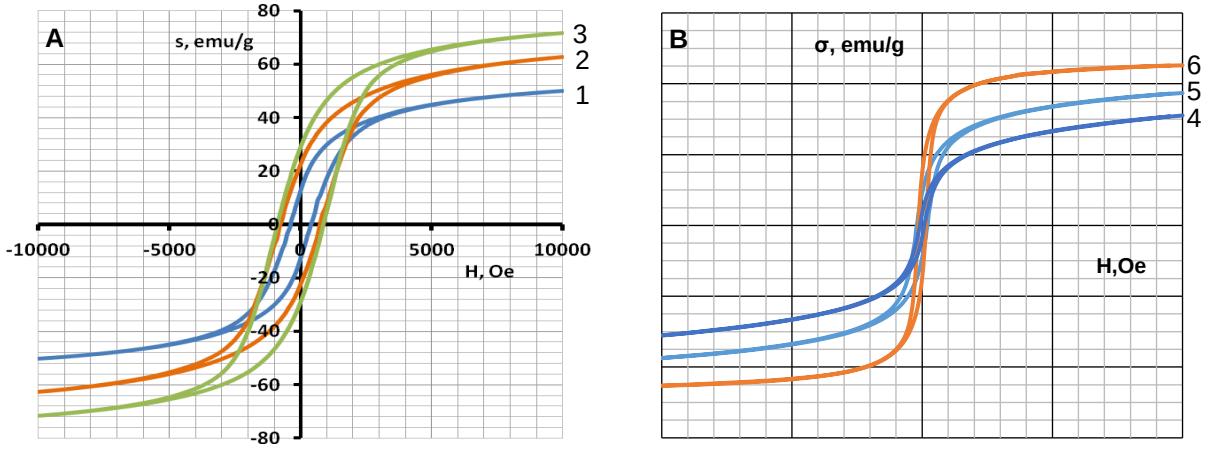

Fig. 5. The magnetic properties of the sample $CoFe_2O_4$ prepared by the hydrothermal synthesis (A) after thermal treatment at 400 °C (1), 600 °C (2) and 800 °C (3) and $NiFe_2O_4$ prepared by the self-combustion synthesis (B) after thermal treatment at 450 °C (4), 650 °C (5) and 850 °C (6).

Conclusions

Single phase nickel and cobalt ferrite nanopowders can be successfully synthesized by the sol-gel self-combustion and hydrothermal synthesis method and high-frequency plasma synthesis.

The magnetic properties of the synthesized ferrite powders depend on their particle size.

The finest ferrite powders were obtained by the hydrothermal synthesis method, whereas ferrites synthesized in plasma had the widest particle size distribution with some particles of 100–200 nm. The presence of such particles probably is the reason for a high saturation magnetization M_S, approaching that of the standard bulk material.

The magnetic properties of samples produced by the sol-gel self-combustion and the hydrothermal synthesis method can be adjusted by changing the particle size by thermal treatment.

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I. Zalite, G. Heidemane, L. Kuznetsova, M. Kodols,
J. Grabis, M. Maiorov

NANOMATMENŲ NIKELIO IR KOBALTO FERITŲ SINTEZĖ IR APIBŪDINIMAS

S a n t r a u k a

Feritai, ypač nikelio ir kobalto, plačiai nagrinėjami dėl savo unikalių mechaninių ir magnetinių savybių. Šiame darbe vienkomponenčiai $NiFe_2O_4$ ir $CoFe_2O_4$ buvo susintetinti trimis būdais: aukšto dažnio plazmos indukuotu cheminiu nusodinimu iš garų fazės, zolių-gelių savaiminio užsiliepsnojimo metodu ir kombinuojant bendrąjį nusodinimą ir hidroterminę sintezę. Nustatytos minėtų junginių magnetinės savybės, apskaičiuotas kristalitų dydis ir savitasis paviršiaus plotas. Nustatyta, kad, sintetinant nikelio ir kobalto feritus aukšto dažnio plazmos indukuotu cheminio nusodinimo iš garų fazės metodu, gautų produktų savitojo paviršiaus ploto vertės kito 28–30 m^2/g (vidutinis dalelių dydis 38–40 nm, kristalitų dydis ~40 nm), o dalelių matmenys vyravo 10–100 nm (kai kuriais atvejais net iki 200 nm). Taikant zolių-gelių savaiminio užsiliepsnojimo metodą ir hidroterminę sintezę, gautų vienkomponenčių nikelio ir kobalto feritų savitieji paviršiaus plotai buvo atitinkamai lygūs 40 ± 3 ir 60 ± 5 m^2/g (vidutinis dalelių dydis 25–30 nm ir 19–26 nm, kristalitų dydis 10–20 nm ir 12–20 nm). Kai degimo temperatūra siekė 900 ºC, minėtų feritų dalelių matmenys didėjo, tačiau jų magnetinės savybės panašėjo į monokristaliniams feritams būdingas savybes.

Reikšminiai žodžiai: $NiFe_2O_4$, $CoFe_2O_4$, nanodalelės, sintezė, savybės.