ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 18, No. 1. 2012

The Synthesis, Characterization and Sintering of Nickel and Cobalt Ferrite Nanopowders

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crossref http://dx.doi.org/10.5755/j01.ms.18.1.1332

Received 09 June 2011; accepted 18 September 2011

The $NiFe_2O_4$ and $CoFe_2O_4$ ferrites were synthesized by two methods – chemical sol-gel self-combustion method and the high frequency plasma chemical synthesis and magnetic properties, crystallite size, specific surface area of synthesized products are characterized. Nanopowders synthesized in the high frequency plasma are with specific surface area in the range of (28 – 30) m^2/g (the average particle size (38 – 40) nm, crystallite size ~40 nm). The ferrite nanopowders obtained by sol-gel self-combustion method have the specific surface area of (37 – 43) m^2/g (average particle size (26 – 31) nm, crystallite size (10 – 20) nm). All synthesized nanopowders were sintered via pressure-less sintering method and magnetic properties of compacted materials were studied, as well.

Keywords: $NiFe_2O_4$, $CoFe_2O_4$, nanoparticles, nanocomposites, properties.

INTRODUCTION

Ferrites are 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]. Meantime, role of ferrite usage for medical, biomedical purposes and also in chemical catalysis are more significant. More information appears about hyperthermia in scientific articles. With this method, ferrite nanoparticles are introduced in living organism and in controlled conditions nanopartices are transported to the cancer zones in organism, and in magnetic field with thermal treatment, cancer cells are eliminated [2].

The properties of nanomaterials varies from its morphology, size and microstructure and it is important to analyze obtaining conditions and method of synthesis of nanoparticles, as well as synthesis of new metal oxides with new properties. Materials, which are used in nanowires, nanosheets, etc., are especially important, because they extend various kinds of optical, electronic and magnetic properties and application limits and quality of products, as well.

Ferrites with spinel structure are significant materials in development of several technological applications, where materials with high density and low porosity are necessary [3]. Ferrites, as most of ceramic materials are obtained in solid phase reactions from different oxides. By improving nanotechnology, several liquid phase and gas phase synthesis have been developed – hydrolysis, hydrothermal synthesis [4], pyrolysis, microwave synthesis [1], co-precipitation method [5], sol-gel method [6], combustion [7] and plasma synthesis [8].

The aim of this research was to obtain nickel and cobalt ferrite nanopowders with two different methods and compare their characteristics as nanopowders and as sintered materials.

EXPERIMENTAL

Two distinct ferrite types ($NiFe_2O_4$ and $CoFe_2O_4$) are obtained by two different methods: by the high frequency plasma chemical synthesis and by the sol-gel self-combustion method.

For production of ferrites by the high frequency plasma chemical synthesis the technological equipment developed in RTU Institute of Inorganic Chemistry was used [8]. Synthesis was realized by evaporating commercial metal and metal oxide (Ni, Co, NiO, CoO and FeO) powders in high frequency plasma to obtain ferrites in Ni-Fe-O and Co-Fe-O systems. All powders in stoichiometric ratio (for resulting products $NiFe_2O_4$ and $CoFe_2O_4$) have been introduced in N_2 plasma with average temperature (5800 – 6200) K. After the powders evaporate, the vapors are very fast cooled with cooling gas (air) and product condensates on filter resulting in nanosized ferrite particles. Parameters of the synthesis are: nitrogen plasma flux – 8 m^3/h, cooling gas (air) flow – 6 m^3/h, generator frequency 5.82 MHz, r.f. oscilator – (56 – 63) kW.

By 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. To 200 mL 0.1 M iron nitrate solution add 100 mL 0.1 M cobalt nitrate (or nickel nitrate) solution. Separately in 100 mL distilled water dissolve glycine and nitric acid, add both to nitrate mixture. Glycine (Gly) is used as the self-combustion agent with molar ratio Me/Gly = 1 : 0.8 and Gly/Nitr. = 1 : 4. Digest the mixture on hotplate and mix evenly with mechanical overhead stirrer

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up to moment when the mixture is congealed. Heat the mixture till it ignites and continues heating 4 h on 300 °C temperature. Ferrite nanopowders (obtained from both methods) where prepared for sintering as follows: 3 wt.% stearic acid mixes mechanically with ferrite nanopowder sample for 1 h in planetary mills (400 rpm, vessel material ZrO_2, milling ball material ZrO_2) by using isopropanol as dispersing environment. Stearic acid is used for better compacting.

After mixing samples were dried in an oven at 80 °C and sieved. For pressure-less sintering samples where pressed (200 MPa) with 12 mm diameter, height (4 – 6) mm. Stearic acid was burned out at 600 °C temperature. Samples were sintered for 2 h at isothermal conditions in air atmosphere at temperature range from (900 – 1200) °C (10 °C/min).

All samples were analyzed by X-ray diffractometer Advance 8 (Bruker AXS). Measuring parameters: CuK_α radiation (1.5418 Å), range (10 – 70) $2\Theta°$, increment 0.02 $2\Theta°$, time per step 1 s, to reduce background effects the SolX detector was used. Crystallite size was determined by the Scherer's equation. Magnetic properties of the synthesized ferrites and nanocomposites were analyzed by vibrating sample magnetometry (VSM Lake Shore Cryotronics, Inc., model 7404 VSM). Specific surface area (SSA) determined with well known BET single point method. Measurements determined at boiling point of liquid nitrogen (–196 °C), adsorbing gas Ar (~7 % Ar gas mixture in He gas).

RESULTS AND DISCUSSION

The characteristics of synthesized ferrite products are given in Tables 1 and 2 and in Figures 1 – 3. It is found that all the synthesized ferrites are nanocrystalline single phase materials with specific surface area of (30 – 40) m^2/g and calculated particle size of (30 – 40) nm.

XRD pattern (Fig. 1) for $NiFe_2O_4$ and $CoFe_2O_4$ nanopowders shows that stoichiometric ferrite nanopowders are obtained. None of obtained XRD patterns show other additional phases (commonly magnetite, maghemite, hematite or other metal oxides), which proves that obtained samples are of high purity.

Analyzing XRD patterns there are slight differences between the relative intensities and width of reflexes comparing ferrite samples depending on synthesis method, which indicates to the differences of crystallite size. The sol-gel self-combustion method gives nanopowders (in both cases – $NiFe_2O_4$ and $CoFe_2O_4$) with smaller crystallite size than nanopowders obtained by the high-frequency plasma synthesis (Table 1).

However the average particle size is not significantly different for nanopowders synthesized by different methods, still comparing sol-gel self-combustion method with plasma synthesized nanopowders there are much greater particle size distribution in range (10 – 100) nm with some particles of 200 nm in the case of plasma powders (Fig. 2).

Nanopowders obtained by plasma synthesis have spheric particles.

Magnetic properties of ferrite nanopowders obtained by both methods are shown in Fig. 3.

The magnetic properties (Fig. 3, Table 2) of nanopowders obtained by the high frequency plasma synthesis are very close to the values of the standard bulk material (the magnetic saturation values are 80 emu/g for $CoFe_2O_4$ and 50 emu/g for $NiFe_2O_4$ [9]).

Table 1. Properties of synthesized ferrite nanopowders

Sample	SSA, m^2/g	d_{50}, nm*	Crystallite size, nm	Phase content
$CoFe_2O_4$ (plasma)	29	39	40	100 % $CoFe_2O_4$
$CoFe_2O_4$ (combust.)	37	31	20	100 % $CoFe_2O_4$
$NiFe_2O_4$ (plasma)	29	38	40	100 % $NiFe_2O_4$
$NiFe_2O_4$ (combust.)	43	26	10	100 % $NiFe_2O_4$

*calculated from SSA.

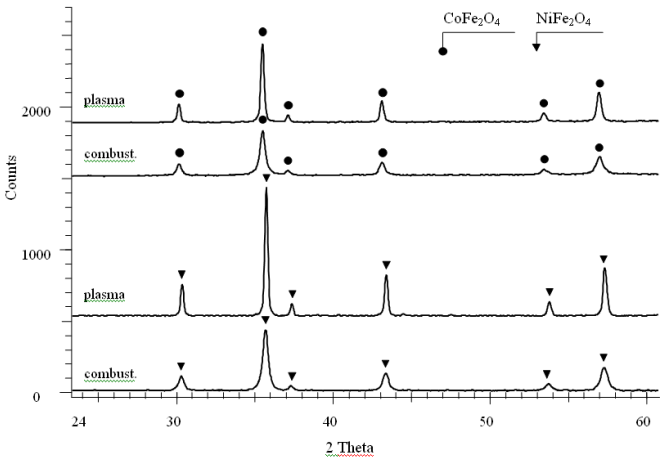

Fig. 1. XRD pattern of ferrite nanopowders

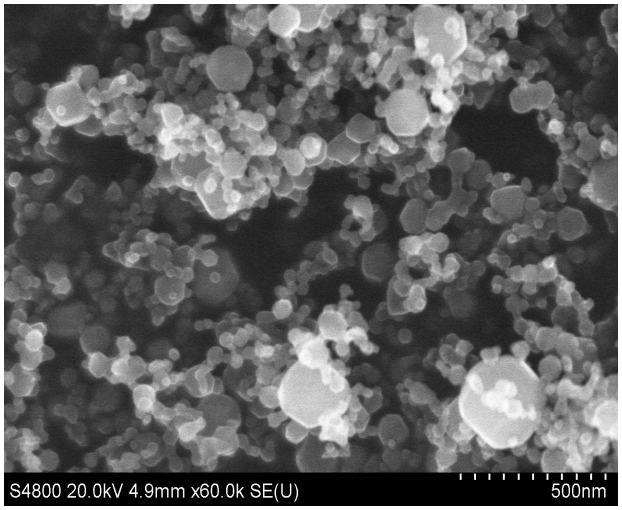

Fig. 2. $CoFe_2O_4$ microstructure, obtained by plasma synthesis

This one proves the high purity of the samples. However, the magnetic properties of the samples obtained by the sol-gel self-combustion method differ from those,

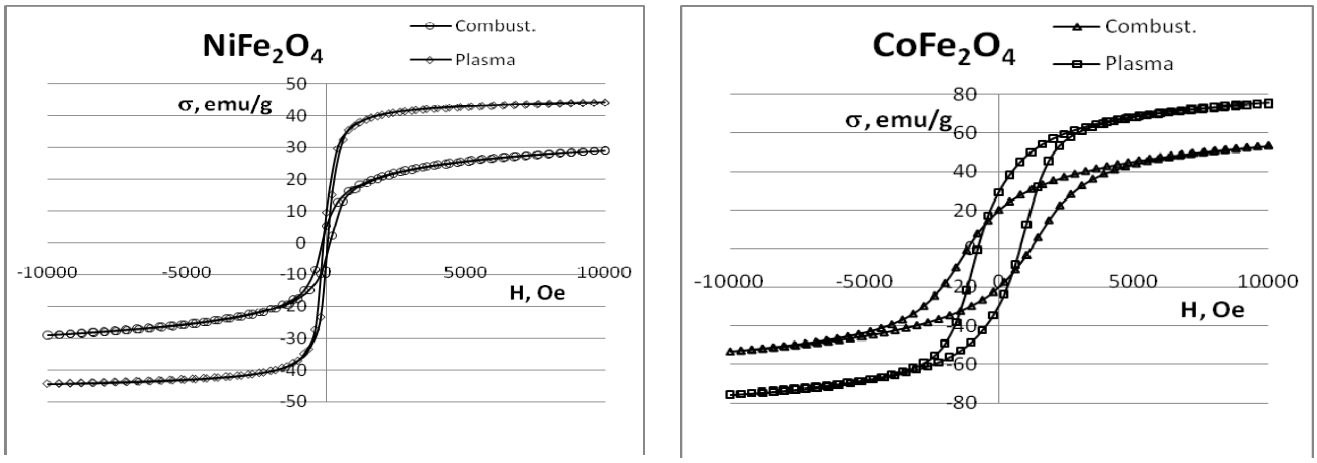

Fig. 3. Magnetic properties of ferrites synthesized by the sol-gel self-combustion method and in plasma

obtained by the plasma synthesis. Probably, it is due to the differences in particle sizes of the nanopowders obtained, by plasma synthesis and sol-gel self-combustion method. Another interesting feature regarding nanopowders synthesized in the framework of this research, are their magnetic behavior, i. e., although all of the nanoparticles, synthesized within the framework of this research, have particle size below the critical single-domain limit (ca. 70 nm [10, 11]), quasi-supermagnetic behavior is observed only in the case of plasma synthesized $NiFe_2O_4$ nanoparticles.

Table 2. Magnetic properties of synthesized ferrite nanopowders

Sample	Saturation magnetization M_S, emu/g	Remanent magnetization M_r, emu/g	Coercivity H_c, Oe
$CoFe_2O_4$ (plasma)	75.4	32.0	780
$CoFe_2O_4$ (combust.)	53.4	20.3	1170
$NiFe_2O_4$ (plasma)	44.2	10.0	74
$NiFe_2O_4$ (combust.)	29.0	6.0	140

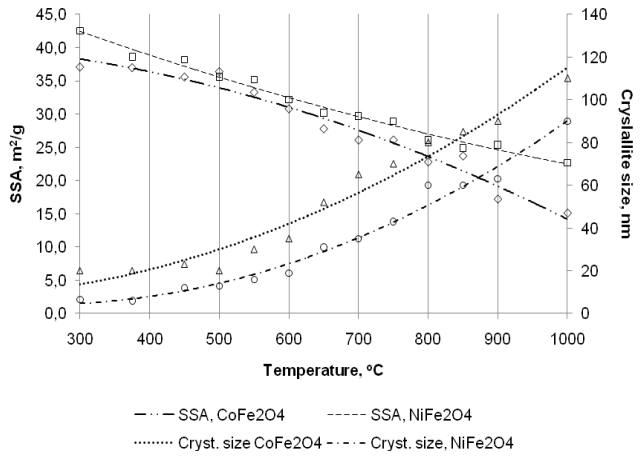

Fig. 4. Specific surface area (SSA) and crystallite size comparison depending on temperature for $NiFe_2O_4$ and $CoFe_2O_4$ synthesized by the sol-gel self-combustion method

After thermal processing the specific surface area of the ferrites synthesized with the sol-gel self-combustion method has a tendency to decrease, while the crystallite size increased. This tendency could be explained that particles are re-crystallizing and growing at higher temperatures, so the specific surface area is decreasing (Fig. 4). With the increase of temperature of thermal treatment, also the saturation magnetization of ferrites increases (Table 3). The relative density before sintering was 50.9 % ($CoFe_2O_4$) and 52.0 % ($NiFe_2O_4$) for plasma synthesized products and 32.6 % ($CoFe_2O_4$) and 31.7 % ($NiFe_2O_4$) for products of sol-gel self-combustion method, percentage from the theoretical values (5.29 g/cm^3 for cobalt ferrite, 5.38 g/cm^3 for nickel ferrite [12]).

Table 3. Magnetic properties of ferrites synthesized by the sol-gel self-combustion method

Samples	Heating temperature, °C	Saturation magnetization M_S, emu/g
$CoFe_2O_4$	450	54.9
	650	75.9
	850	79.9
	900	79.8
$NiFe_2O_4$	450	21.4
	650	37.4
	850	45.2
	900	47.4

This shows that ferrite nanopowders obtained by the sol-gel self combustion method are more difficult to press because of their small particles comparing with plasma synthesized ferrites.

Sintering was made at 900 °C, 1000 °C, 1100 °C and 1200 °C temperatures and ferrite density after thermal processing is shown in Table 4.

Table 4. The relative density and open porosity of ferrites depending on temperature

Sample	Sintering temperature, °C							
	900		1000		1100		1200	
	Density, %	Open porosity, %	Density, %	Open porosity, %	Density, %	Open porosity, %	Density, %	Open porosity, %
$CoFe_2O_4$ (plasma)	82.6	16.0	97.0	0.2	98.5	0.1	97.9	0
$CoFe_2O_4$ (combust.)	–	–	65.7	34.4	78.3	21.6	93.4	3.1
$NiFe_2O_4$ (plasma)	87.9	12.1	99.4	0.2	100.0	0.2	100.0	0
$NiFe_2O_4$ (combust.)	–	–	72.4	25.5	87.7	9.4	96.1	1.6

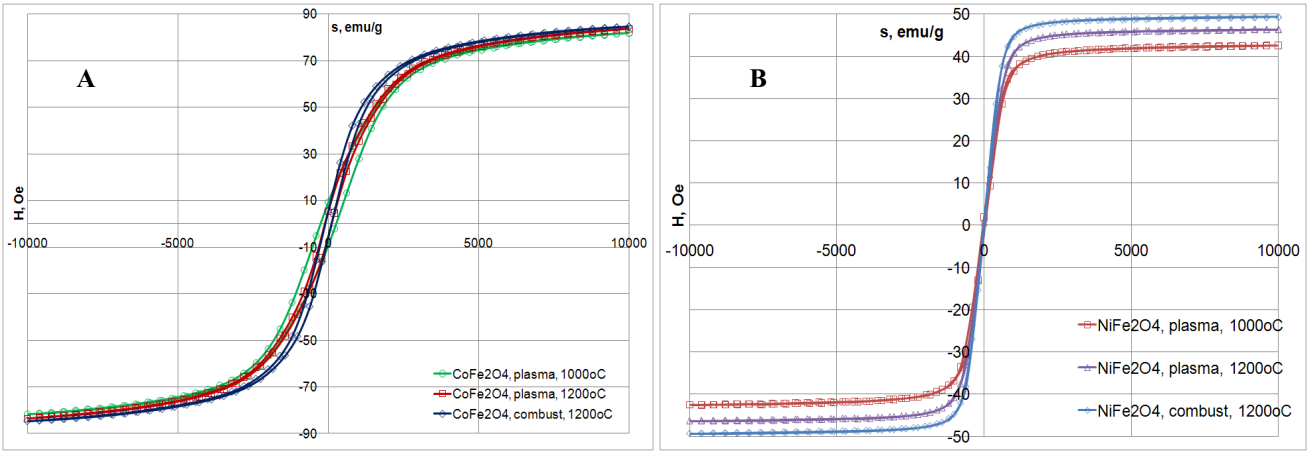

Fig. 5. Magnetic properties of $CoFe_2O_4$ (A) and $NiFe_2O_4$ (B) ferrite, sintered in 1200 °C

By increasing the sintering temperature, the size of nanoparticles is growing and magnetization for both ferrite nanomaterials are also increasing, while coercivity is decreasing (Fig. 5). Comparing to ferrite nanopowders, especially obtained by the sol-gel self combustion method, the sintered materials have higher magnetization and lower coercivity, which could be explained with particle size and also crystallite size. However, particle size causes magnetization and so sintered materials have better magnetic properties than nanopowders.

CONCLUSIONS

Single phase nickel and cobalt ferrite nanopowders can be successfully synthesized by the sol-gel self-combustion method and high-frequency plasma, as well. The average particle size of nanopowders obtained by the sol-gel self-combustion method is in the range (25 – 40) nm and ferrites synthesized in plasma have wider particle size distribution in range (10 – 100) nm with some particles of 200 nm. The magnetic saturation values of these samples are very close to the values of the standard bulk material (80 emu/g for $CoFe_2O_4$ and 50 emu/g for $NiFe_2O_4$). However, the magnetic properties of the samples obtained by the sol-gel self-combustion method differ from those of the plasma products; this is probably concerned with crystallite size.

The compact materials have been obtained by the pressure-less sintering method. Dense material from the plasma nanopowders forms at 1000 °C, but from the sol-gel self-combustion nanopowders at 1200 °C. Comparing to nanopowders, the sintered materials have higher magnetic properties and this tendency is more characteristic for nanopowders which were synthesized by the sol-gel self-combustion method.

Acknowledgments

The research was made due to financial support of the European Structural Funds (Project No. 2009/0215/1DP/ /1.1.1.2.0/09/APIA/VIAA/082).

REFERENCES

1. **Xue, B., Liu, R., Xu, Z. D, Zheng, Y. F.** Microwave Fabrication and Magnetic Property of Hierarchial Spherical Fe_2O_3 Nanostructures *Chemistry Letters* 37 (10) 2008: pp. 1058 – 1059. http://dx.doi.org/10.1246/cl.2008.1058
2. **Fortin, J. P., Wilhelm, C., Servais, J., Menager, C., Bacri, J. C. F., Gazeau, J.** Size Sorted Anionic Iron Oxide Nanomagnets as Colloidal Mediators for Magnetic Hyperthermia *Chemical Society* 129 2007: pp. 2628 – 2635.
3. **Domenichini, B., Caillot, T.** Sintering of Fe_2NiO_4 with Internal Binder: a Way to Obtain a Very Dense Material *Acta Material* 51 2003: pp. 4815 – 4821.

4. **Millot, N., Gallet, S. L., Aymes, D., Bernard, F., Grin, Y.** Spark Plasma Sintering of Cobalt Ferrite Nanopowders Prepared by Coprecipitation and Hydrothermal Synthesis *Journal of European Ceramic Society* 27 2007: pp. 921 – 926.
5. **Ferreira, T. A. S., Waerenborgh, J. C., Mendonça, M. H. R. M., Nunes, M. R., Costaa, F. M.** Structural and Morphological Characterization of $FeCo_2O_4$ and $CoFe_2O_4$ Spinels Prepared by a Coprecipitation Method *Solid State Sciences* 5 2003: pp. 383 – 392.
6. **Tang, D. Q., Zhang, D. J., Ai, H.** Fabrication of Magnetic Core-shell $CoFe_2O_4/Al_2O_3$ Nanoparticles as Immobilized Metal Chelate Affinity Support for Protein Adsorption *Chemistry Letters* 35 (11) 2006: pp. 1238 – 1239.
7. **Zhongpo, Z., Yue, Z., Ziyu, W., Wei, W., Wufeng, T., Jing, S., Rui, X.** Electronic Structure Studies of the Spinel $CoFe_2O_4$ by X-ray Photoelectron Spectroscopy *Applied Surface Science* 254 2008: pp. 6972 – 6975.
8. **Grabis, J., Zalite, I.** Nanosize Powders of Refractory Compounds for Obtaining of Fine-grained Ceramic Materials *Materials Science Forum* 555 2007: pp. 267 – 272.
9. **Smit, J., Wijn, H. P. J.** In: Ferrites. Philips Technical Library. Eindhoven, Netherlands, 1959.
10. **Cornell, R. M., Schwertmann, U.** In: The Iron Oxides. Structure, Properties, Reactions, Occurrences and Uses. Wiley-VCH, Weinheim, 2003.
11. **Song, Q., Zhang, Z. J**. Correlation between Spin-orbital Coupling and the Superparamagnetic Properties in Magnetite and Cobalt Ferrite Spinel Nanocrystals *Journal of Physical Chemistry B* 110 2006: pp. 11205 – 11209.
12. **du Tremolet, E., de Lacheisserie, E., Ginoux, D., Schlenker, M.** In: Magnetism Fundamentals. Springer Link, New York, 2005.

Presented at the 20th International Conference "Materials Engineering'2011"
(*Kaunas, Lithuania, October 27 – 28, 2011*)