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Properties of Nanosized Ferrite Powders and Sintered Materials Prepared by the Co-Precipitation Technology, Combined with the Spray-Drying Method

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Abstract. Cobalt and nickel ferrites powders are synthesized by the co-precipitation technology, combined with the spray-drying method. The crystallite size, specific surface area (SSA), magnetic properties of synthesized products are investigated. All the synthesized ferrites are nanocrystalline single phase materials with crystallite size of 5-6 nm, the SSA of 80-85 m^2/g and the calculated particle size of 13-15 nm. After spray-drying granules of the size up to 10 μm are obtained. After thermal treatment at 550 and 950 °C SSA decreases to 40-50 m^2/g and 20-22 m^2/g, respectively. The saturation magnetization at these temperatures increase from 17 to 40 emu/g for $NiFe_2O_4$ and from 51 to 77 emu/g for $CoFe_2O_4$. By the pressure-less sintering method the dense material forms at 1100 °C for $CoFe_2O_4$ and 1200-1300 °C for $NiFe_2O_4$.

Introduction

Ferrites are widely applied in life sciences, biochemical processes (magnetic liquids, hyperthermia etc.), in chemical catalysis and special coatings (antistatics, electromagnetic interference shielding). The effectiveness of the spinel ferrites in most of these applications can be increased, if their dimensions are in nanolevel, i.e., below single domain sizes [1]. Properties of ferrites, can be tailored also depending on it morphology and nanostructure. Consequently, it is important to analyse the effects of manufacturing methods/conditions on structural features of ferrite nanoparticles.

Several liquid phase and gas phase synthesis have been developed to synthesize ferrite nanoparticles – microwave synthesis [1], hydrothermal synthesis [2], hydrolysis, pyrolysis, sol-gel method [3], combustion [4] and plasma synthesis [5]. One of these is the co-precipitation method [6]. Main disadvantage of classic co-precipitation method is difficult and slow precipitation stage of obtained hydroxides. We have produced ferrite nanopowders by the co-precipitation technology, combined with the hydrothermal synthesis method [7].

In this research the co-precipitation synthesis is combined with the treatment of the obtained suspension by the spray-drying method with the following thermal treatment of granules, and structure and magnetic properties of these ferrites have been studied.

Experimental

Synthesis of nickel and cobalt ferrite nanoparticles was performed by the co-precipitation technology, combined with the spray-drying method and thermal treatment at different (350-950 °C) temperatures. By this method ferrites were synthesized using reagent grade chemicals: $FeCl_3 \cdot 6H_2O$, urea, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, NaOH [7]. Precursor was obtained as follows: urea was hydrolysed for 3 hours in the solution of $FeCl_3$ (molar ratio 3:1) at 70-75 ^oC. 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. Stirring the suspension continuously with the 40% solution of NaOH, cobalt or nickel hydroxide is slowly precipitated until the pH of suspension is of 9-10, then inserted in the ultrasound bath for 20 min. and after it treated for 24 h at 40 ^{o}C. After the precipitate was washed decanting with distilled water until the presence of Cl^- ion has not been registered.

The equipment for granulation and spraying of nanopowders by the drying method developed at the Institute of Inorganic Chemistry of the RTU was used for spraying of the hydroxide mixture. The main parameters of the suspension spraying: temperature of hot air – 370 ^{o}C, consumption – 24 m^3/h, temperature in the evaporation chamber – 120-130 ^{o}C.

Ferrite nanopowders were prepared for sintering as follows: 3 wt.% stearic acid was mixed mechanically with the ferrite nanopowder sample for 1 h in the planetary mills (400 rpm, vessel material ZrO_2, milling ball material ZrO_2) by using isopropanol as dispersing medium. After mixing samples were dried in an oven at 80 °C and sieved. For pressure-less sintering samples were pressed (200 MPa) in pellets with diameter of 12 mm and 4 - 6 mm in height. Stearic acid was burned out at 600 °C. Samples were sintered for 2 h isothermally in air at the temperature range from 1000 – 1300 °C (10 °C/min) in the furnace LHT-08/18 (Nabertherm GmbH).

All samples were analysed by the X-ray diffractometer Advance 8 (Bruker AXS). Crystallite size was determined by the Scherer's equation. Magnetic properties of the synthesized ferrites were analysed by vibrating sample magnetometry (VSM Lake Shore Cryotronics, Inc., model 7404 VSM). Specific surface area (SSA) was measured by the BET single point method. The size and morphology of particles as well as the microstructure of the sintered material were observed by the scanning electron microscopy (SEM) (Mira/Tescan) on fracture surfaces. The density of the sintered samples was determined by the Archimedes method.

Results and discussion

The characteristics of synthesized ferrites are given in Table 1 and in Figures 1-4. In the case of spray-drying high dispersity nanoparticles were obtained, consisting mainly of cobalt or nickel ferrite, iron hydroxide FeO(OH) and X-ray amorphous part of sample. The SSA was in a wide scope of 80-90 m^2/g (Table 1). After spray-drying granules of size up to 10 μm (Fig. 1.) and calculated average particle size of them of 13-15 nm were obtained.

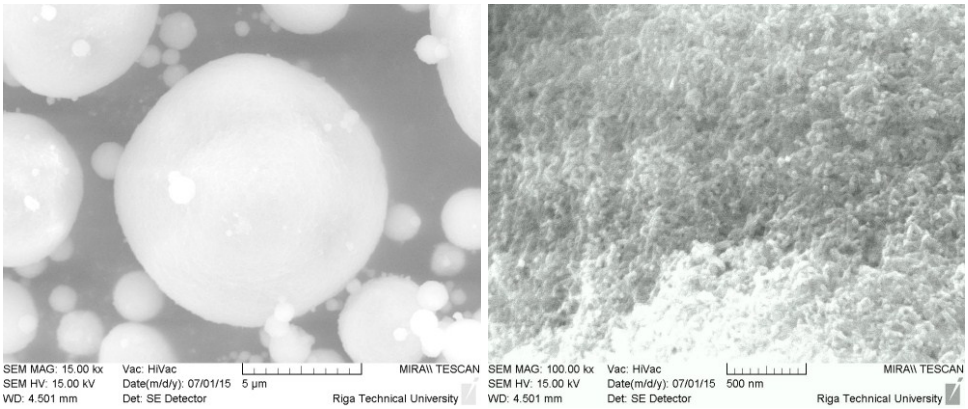

Fig. 1. The electron microscope images of spray-dried $NiFe_2O_4$ at different enlargements.

After thermal treatment, starting from 350 °C, the single phase product ($NiFe_2O_4$ or $CoFe_2O_4$) with the SSA from 100 (at 350 °C) to 20 m^2/g (at 950 °C) was obtained (Fig. 2.). The saturation magnetization (Ms) of $NiFe_2O_4$ and $CoFe_2O_4$ rises from 6 and 15 emu/g (at 450 °C) to 40 and 77 emu/g (at 950 °C), resp. (Fig. 3.). This could be due to an increase in crystallite size.

After thermal treatment, starting at 450 ºC, nanocrystalline stoichiometric single phase powders form (Fig. 4.). None of the XRD patterns of samples obtained at optimal synthesis conditions shows other additional phases (commonly magnetite, maghemite, hematite or other metal oxides), which proves that they are of high purity.

Table 1. Properties of synthesized $CoFe_2O_4$ and $NiFe_2O_4$ nanopowders after thermal treatment (2 h at different temperature)

Sample	Tempera-ture [ºC]	SSA [m^2/g]	d_{50}* [nm]	Crystallite size [nm]	Phase composition	Ms [emu/g]	Mr [emu/g]	Hc [Oe]
$NiFe_2O_4$	raw powder	85,1	14	-	p.a., $NiFe_2O_4$, FeO(OH)	-	-	-
	350	99,8	13	4 (p.a.)	p.a., $NiFe_2O_4$	-	-	-
	550	39,9	28	9	$NiFe_2O_4$	16,9	1,1	56,5
	750	29,2	38	19	$NiFe_2O_4$	21,6	4,5	214,2
	950	22,0	51	58	$NiFe_2O_4$	40,0	8,6	150,9
$CoFe_2O_4$	raw powder	83,9	14	-	p.a.,$CoFe_2O_4$, FeO(OH)	-	-	-
	350	76,8	15	6	p.a., $CoFe_2O_4$	-	-	-
	550	51,1	22	15	$CoFe_2O_4$	51,3	14,7	648,5
	750	35,4	32	24	$CoFe_2O_4$	61,1	22,3	877,6
	950	21,3	53	66	$CoFe_2O_4$	76,8	34,1	1067,4

* average particle size calculated from SSA; p.a. – partially amorphous
Ms - saturation magnetization, emu/g; Mr - remanent magnetization, emu/g; Hc – coercivity, Oe

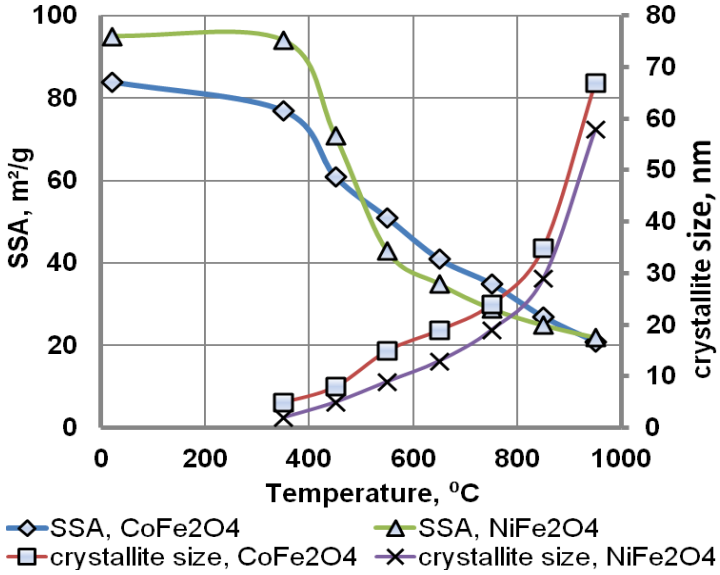

Fig. 2. Specific surface area (SSA) and crystallite size comparison depending on temperature for $NiFe_2O_4$ and $CoFe_2O_4$.

To find, how the crystallization degree of starting powder effects the density, crystallite size and magnetic properties of the sintered material, the sintering of thermally not treated powders and powders calcinated at 650 °C for 2 h was made. The sintering of nanosized $CoFe_2O_4$ and $NiFe_2O_4$ powders was made at 1000, 1100, 1200 and 1300 °C temperature and ferrite density after thermal processing is shown in Table 2.

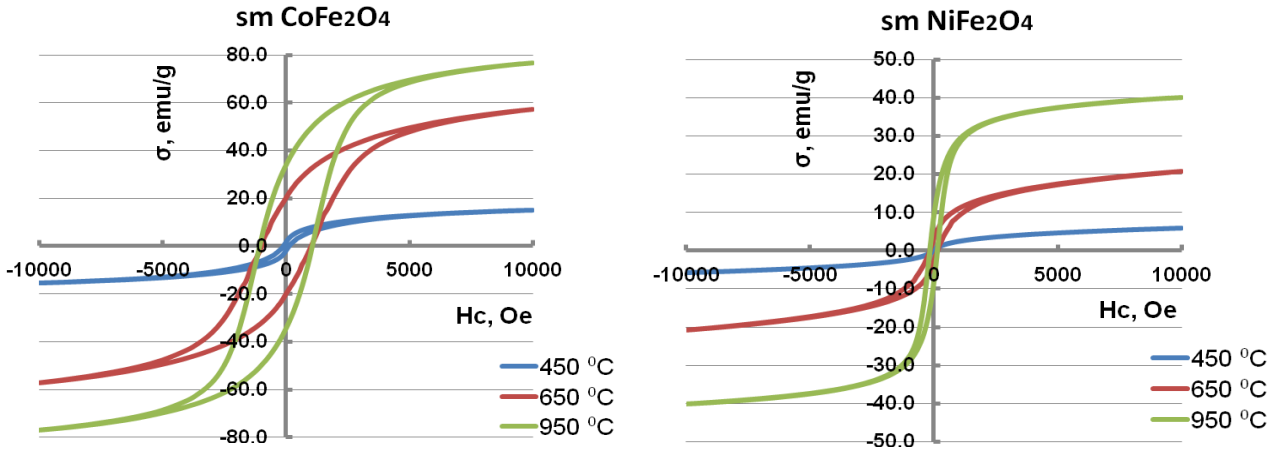

Fig. 3. The magnetic properties of the sample $CoFe_2O_4$ and $NiFe_2O_4$ after thermal treatment at 450, 650 and 950 °C.

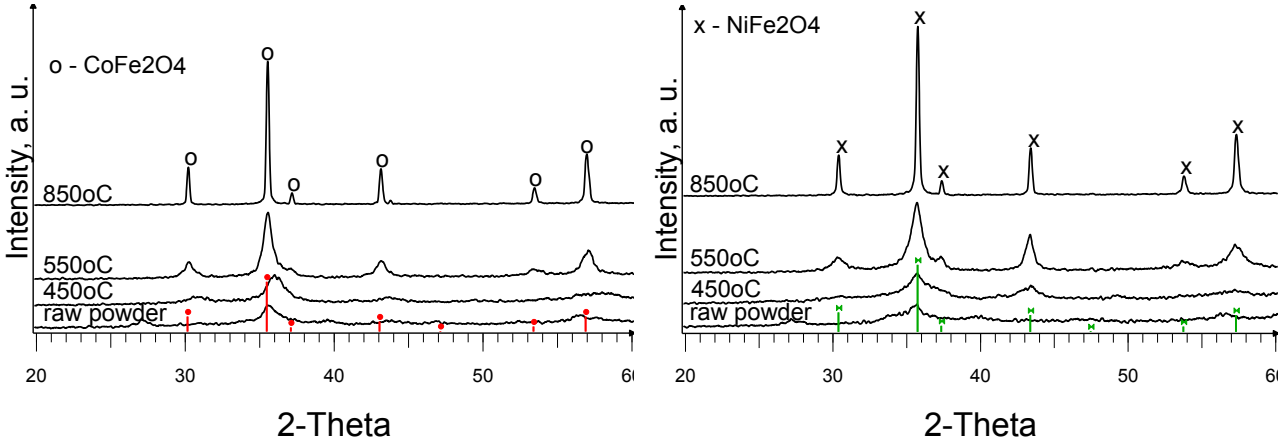

Fig. 4. XRD pattern of „spray-drying" ferrite nanopowders.

Table 2. The relative density and open porosity of the sintered ferrites depending on temperature

Sample	Sintering temperature [°C]							
	1000		1100		1200		1300	
	Density [%]	Open porosity [%]	Density [%]	Open porosity [%]	Density [%]	Open porosity [%]	Density [%]	Open porosity [%]
$CoFe_2O_4$	62,3	35,5	90,0	8,8	90,8	4,7	95,1	0,7
$CoFe_2O_4$-650/2	72,1	26,0	89,6	8,5	93,8	0,5	94,9	0,3
$NiFe_2O_4$	52,2	44,0	69,5	27,6	85,3	12,1	90,7	7,1
$NiFe_2O_4$-650/2	69,9	27,4	81,4	15,6	91,3	6,0	93,5	1,4

It was found, that the previous treatment of powders does not affect properties of sintered material significantly. They depend more on sintering temperature – if the temperature is higher, the density and grain size of material increases, by the following increase of magnetic properties. Comparatively dense material forms at 1100 °C for $CoFe_2O_4$ and 1200-1300 °C for $NiFe_2O_4$. The crystallite size during sintering grows a few: from 70-80 nm at 1100 °C up to 120-140 nm at

1300 °C. The grain size for samples sintered at 1200°C does not exceed 2 μm for Co ferrite and 5 μm for Ni ferrite (Fig.5.). The saturation magnetization of samples sintered at this temperature reaches 79 emu/g for $CoFe_2O_4$ and 48 emu/g for $NiFe_2O_4$.

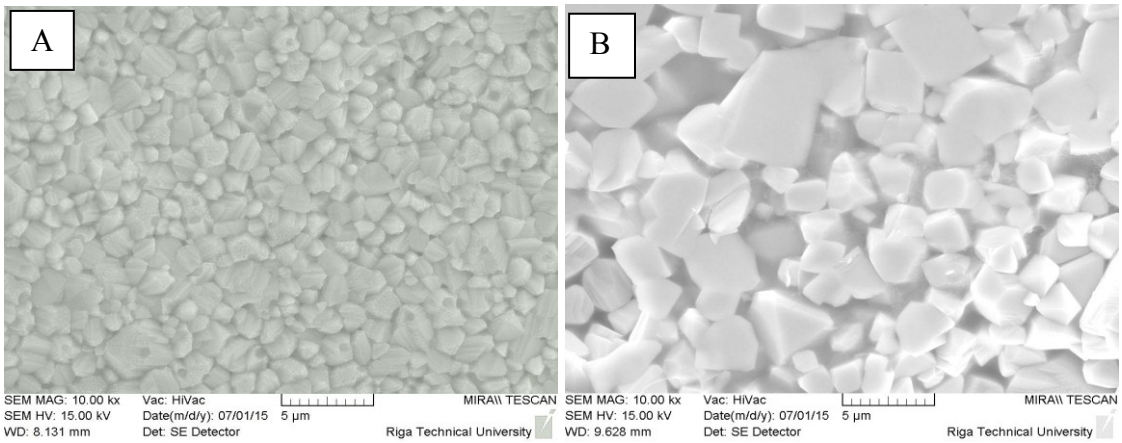

Fig. 5. Microphotos of $CoFe_2O_4$ (A) and $NiFe_2O_4$ (B) ceramics sintered at 1200 ºC.

Summary

Single phase Ni and Co ferrite nanopowders were successfully synthesized by the modified co-precipitation synthesis with "spray-drying" method. The average particle size of obtained nanopowders is in the range of 15-55 nm, depending on thermal treatment temperature (TTT). Magnetic properties of the synthesized ferrite powders depend on the TTT: saturation magnetization values 6-40 emu/g for $NiFe_2O_4$ and 15-77 emu/g for $CoFe_2O_4$, at 550 and 950 °C, respectively.

The compact materials have been obtained by the pressure-less sintering method. Relatively dense material forms at 1100 °C for $CoFe_2O_4$ and 1200-1300 °C for $NiFe_2O_4$. The sintered materials have slightly higher magnetic properties compared with nanopowders.

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