MAGNETIC FERRITE NANOPARTICLES WITH INCREASED MAGNETIZATION AND CRYSTALLINITY BY SPRAY-DRYING WITH NaCl AND SUBSEQUENT THERMOLYSIS

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Nanosized magnetic particles based on iron oxides are of great importance for a wide area of applications: sensors, catalysts, sorbents, magnetic dug delivery, magnetic resonancy imaging, etc. Lots of these applications require non-agglomerated particles with a large surface area and average diameter below 50 nm. However, such particles exhibit quite low specific magnetization as compared to bulk materials due to the surface spin disorder of surface atoms [1]. Many conventional methods of magnetic nanoparticle synthesis, such as coprecipitation, spray pyrolysis and reverse micelle synthesis, require additional thermal treatment to increase crystallinity and specific magnetization of the particles [2]. The main problem of this approach is a significant increase of particle size as a result of annealing.

In this work, zinc-substituted cobalt and magnesium ferrite nanoparticles were prepared by coprecipitation from water solution of corresponding nitrates. The resulting suspensions were mixed with NaCl and then spray-dried at 200 °C using Labultima–222 ADVANCED Laboratory Spray Dryer. The powders obtained were then annealed at 300-900 °C to increase specific magnetization of nanoferrites. The isolating layer of NaCl formed between the particles during spray-drying prevented them form aggregation and sintering during annealing. After the annealing, NaCl matrix was removed by washing with deionised water. The difference between this approach and spray pyrolysis in presence of NaCl is lower spraying temperature (200 °C for spray-drying vs. 500-700 °C for pyrolysis), which makes it easier and more cost-efficient [3].

Structural, morphological and magnetic properties of the resulting nanoparticles were investigated by XRD, SEM, TEM, FT-IR spectroscopy and SQUID magnetometry. After spray-drying, ferrite nanoparticles and NaCl form hollow spheres with an average diameter of 1-5 µm, while the size of single nanoparticles is ~5-10 nm. Average crystallite size calculated from XRD data, as well as particle diameter measured from TEM, does not increase significantly up to 700 °C and does not exceed 10 nm. Further raise of annealing temperature to 900 °C leads to intense recrystallization and therefore increase of particle size to 40-60 nm (major fraction). Specific magnetization of the ferrites was found to increase with the increase of annealing temperature – from 31.5 to 91.3 emu/g for $Co_{0,65}Zn_{0,35}Fe_2O_4$ and from 4.69 to 22.31 for $Mg_{0,5}Zn_{0,5}Fe_2O_4$ annealed at 300 and 900 °C, respectively. This might be caused by cation redistribution between spinel sublattices of ferrites, which is proved by changes in lattice parameter *a* (Table 1). Another reason is the structure ordering, decrease of defect concentration and increase of crystallinity of nanoparticles with the increase of temperature due to recrystallization.

Table 1. Structural and magnetic properties of the ferrite nanoparticles annealed at different temperatures: lattice parameter a, average crystallite size d_{XRD}, specific magnetization M (measured at 0.86 T) and crystallinity degree

T, °C	$Co_{0,65}Zn_{0,35}Fe_2O_4$				$Mg_{0,5}Zn_{0,5}Fe_2O_4$			
	a, Å	d_{XRD}, nm	M, emu/g	Crystallinity degree, %	*a*, Å	d_{XRD}, nm	M, emu/g	Crystallinity degree, %
300	8.344	5.54	31.5	87.20	8.429	3.73	4.69	66.17
500	8.355	6.74	44.2	90.39	8.408	4.46	17.76	82.05
700	8.406	8.01	58.9	91.73	8.437	10.60	-	72.92
900	8.406	30.91	91.3	98,76	8.420	34.23	22.31	89.62

All the particles exhibit superparamagnetic behavior with no coercivity at room temperature, and their average size does not exceed 100 nm even after annealing at 900 °C. This proves the method described to be effective for producing non-agglomerated nanosized ferrites with increased magnetization and crystallinity.

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