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Synthesis and magnetic properties of $Co_{1-x}Zn_xFe_2O_{4+\gamma}$ nanoparticles as materials for magnetic fluid hyperthermia

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ABSTRACT

Nanoparticles of the single spinel phase $Co_{1-x}Zn_xFe_2O_{4+\gamma}$ of mean size 3–23 nm, as determined by X-ray diffraction analysis, were synthesized by the co-precipitation method followed by a temperature treatment. Magnetic studies carried out in the range of 4.5–550 K revealed gradual transition from ferrimagnetic to superparamagnetic to paramagnetic behaviour depending on the composition and particle size. The observed behaviour indicates a broad distribution of volume sizes of the nanoparticles. Particular importance can be ascribed to the composition of $x=0.6$ where the observed transition temperature to the paramagnetic state at 310–334 K suggests applicability of this material for magnetic fluid hyperthermia in a self-controlled regime.

1. Introduction

Currently magnetic nanoparticles have been attracting increasing interest because of a large variety of applications in medicine, like as materials for magnetic fluid hyperthermia. Meanwhile, used hybrid nanoparticles are, however, nearly exclusively based on cores of magnetite Fe_3O_4 and maghemite γ-Fe_2O_3, of properties uneasily adjustable in a desired way. Therefore attention is nowadays focused on complex magnetic oxides of parameters more easily modifiable. In this context, cobalt ferrite, $CoFe_2O_4$, was studied e.g. in [1–5].

Cobalt ferrite possesses a partially inverse spinel structure of the formula $(Co_\delta Fe_{1-\delta})^A[Co_{1-\delta}Fe_{1+\delta}]^BO_4$, where A and B indicate tetrahedral and octahedral sites, respectively. The resulting magnetic moment is given by the antiparallel ferrimagnetic arrangements of the prevailing ionic spins in the B sublattice and the less populated spins in the A sublattice. The magnetic properties are significantly influenced by a remarkably high magnetocrystalline anisotropy, assuring the stability of the magnetic ordering with decrease in crystallite size. Therefore only a moderate decrease of the bulk values of the saturated magnetization $M_s \sim 95$ A m^2 kg^{-1} down to $M_s \sim 56$–58 A m^2 kg^{-1}, of the Curie temperature $T_c = 790$ K down to $T_c = 735$ K for nanoparticles of mean size $\sim$15 nm and the critical size for the transition to superparamagnetic state at $\sim$5 nm around room temperature are observed. Besides that the coercivity and remanent magnetization, parameters of a crucial importance for the shape of the hysteresis loops and consequently for the heating efficiency if magnetic fluid hyperthermia application is considered, can be additionally controlled by varying the crystallite size [1,6–8].

Properties of cobalt ferrite can be further modified by a suitable compositional variation, e.g. by partial replacement of the cobalt cations by non-magnetic zinc cations. The mechanism of the substitution is described by the formula $(Zn_x^{2+}Fe_{(1-x)}^{3+})^A[Co_{(1-x)}^{2+}Fe_{(1+x)}^{3+}]^BO_4$, taking into account the strong preference of zinc ions for tetrahedral sites. It is valid for bulk materials while for nanoparticles simultaneous presence of zinc ions in octahedral sites was recently reported by several authors [9–12]. Our original results aimed at this question were recently presented as a

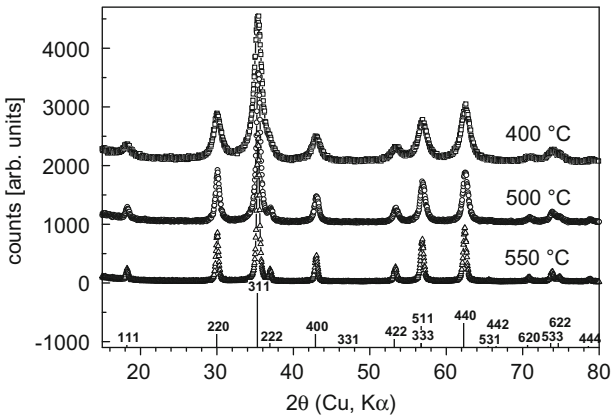

Fig. 1. Indexed diffraction patterns of the spinel phases $Co_{0.4}Zn_{0.6}Fe_2O_{4+\gamma}$.

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Table 1
The mean crystallite size d_{XRD}, blocking temperature T_B and Curie temperature T_c of the nanoparticles of the ferrites $Co_{1-x}Zn_xFe_2O_{4+\gamma}$ annealed at various temperatures.

x	$T_{annealing}$ (K)	d (nm)	T_B (K)	T_c (K)
0.7	400	3	78	216
0.7	500	14	133	237
0.7	550	23	52, 139	216
0.6	400	3	143	310
0.6	500	13	194	334
0.6	550	24	210	317
0.5	400	7	191	410
0.5	500	15	240	420
0.5	550	22	282	410

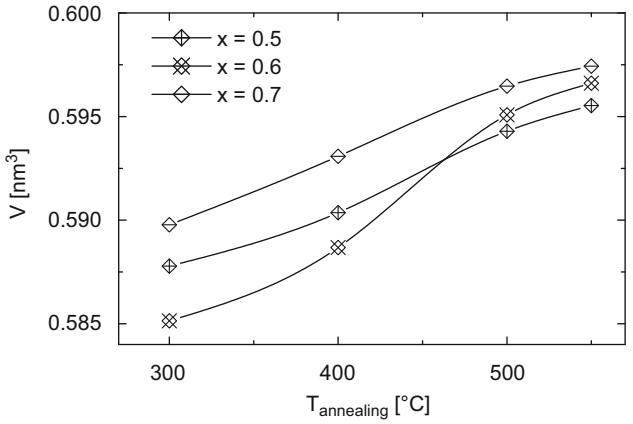

Fig. 2. Dependence of the crystal cell volume [nm^3] of the samples $Co_{1-x}Zn_xFe_2O_{4+\gamma}$, $x \in \langle 0.5, 0.7 \rangle$, on the temperature of annealing.

conference contribution [13] and will be reported in details elsewhere. The total moment increases with the Zn doping practically linearly in the region $0 \le x \le 0.5$, as expected for decreasing population of magnetic ions in the A sublattice [14]. Nonetheless, the continuing decrease of the concentration of magnetic ions in the tetrahedral positions ($x > 0.5$) causes a weakening of the A–B interactions and thus leads to a disturbance of the spin ordering causing a drop of total moment for ($x > 0.5$) and, finally, destabilization of the ferrimagnetic ordering [15].

As a result the outlined effects offer in a selected range of $0.5 \le x \le 0.7$ of the $Co_{1-x}Zn_xFe_2O_4$ solid solutions a possibility of tuning suitably the magnetic parameters, i.e. Curie temperature, magnetization and coercivity, to the values assuring simultaneously a reasonable heating efficiency and the self-controlled heating mechanism in the range of ~40–60 °C [16–18]. Therefore we attempted in the present study to synthesize cobalt–zinc ferrite nanoparticles in a suitable composition range and to determine their fundamental magnetic characteristics giving a chance to gain cores materials with parameters appropriate for magnetic fluid hyperthermia.

2. Experimental stage

2.1. Synthesis

Synthesis of ferrites was carried out by the co-precipitation method followed by a temperature treatment. The analyzed materials, Co (II), Zn (II) and Fe (III) nitrates (purity grade p.a.), were dissolved in water and mixed together in appropriate proportions of cations, corresponding to the chemical formula $Co_{1-x}Zn_xFe_2O_4$ (x: 0.5, 0.6 and 0.7). Then by an addition of the ammonium hydroxide the pH factor of the solution was adjusted

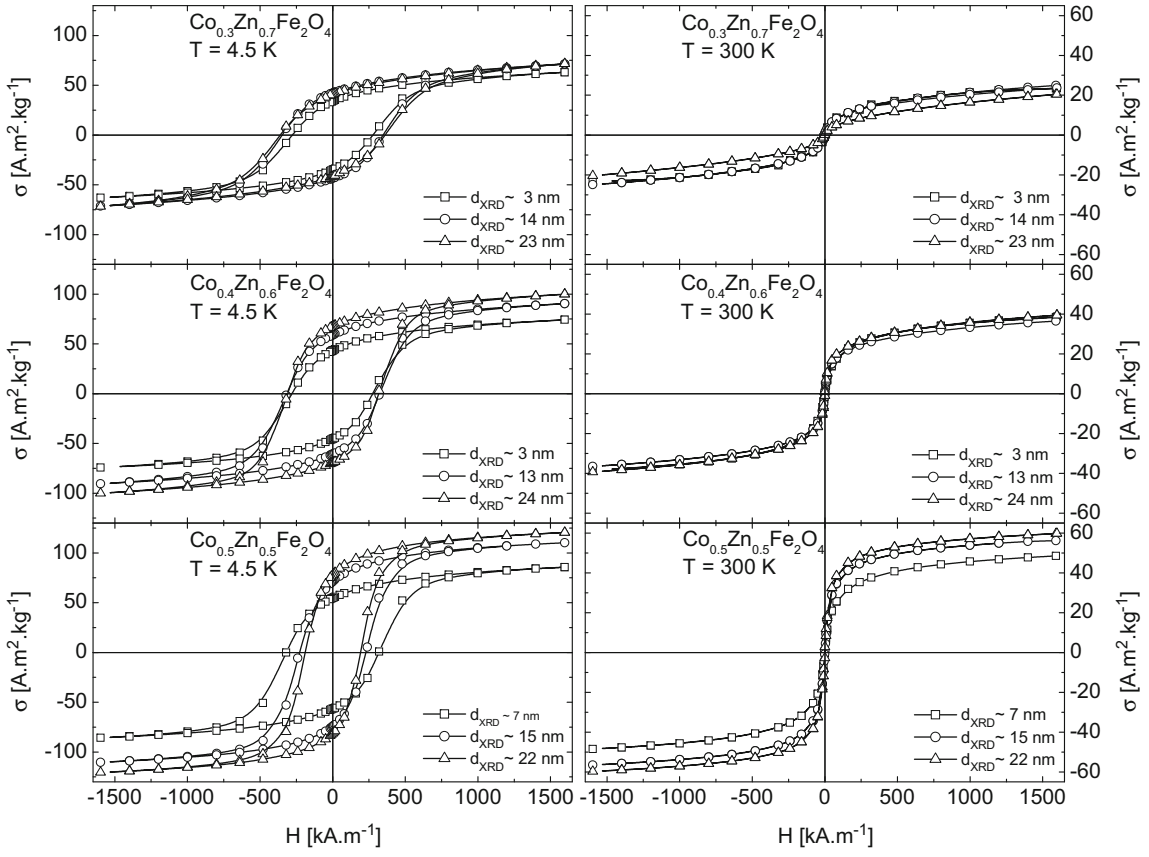

Fig. 3. Magnetization loops measured at temperatures 4.5 and 300 K for different compositions and crystallite sizes of the Co–Zn ferrites.