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Study of magnetic and structural properties of cobalt-manganese ferrite nanoparticles obtained by mechanochemical synthesis

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HIGHLIGHTS

- Cobalt-manganese nanoferrites were obtained by mechanochemical synthesis.
- Addition of sodium chloride resulted in the increase of the nanoparticle size.
- The influence of the mechanochemical synthesis conditions was investigated.

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ABSTRACT

Cobalt-manganese ferrites were synthesized by the mechanochemical synthesis using metal salts as a precursor and sodium chloride as a growth agent. The dependence of the size and the magnetic properties of the prepared nanoparticles on the high-energy ball milling conditions were investigated. Cobalt-manganese ferrite nanoparticles were characterized using the Mössbauer spectroscopy, atomic force microscopy (AFM) and X-ray diffraction. Measurements showed that the particle size of the cobalt ferrite nanoparticles varied from 4 nm up to ~10 nm without and with the addition of sodium chloride respectively whereas no such effect of the sodium chloride on manganese nanoparticles was observed.

1. Introduction

Superparamagnetic ferrite nanoparticles have been extensively studied because of their good magnetic, catalytic properties, excellent chemical stability and therefore used in ferrofluids, information storage and chemical technology. In the recent years, $CoFe_2O_4$ and $MnFe_2O_4$ nanoparticles were investigated for the biomedical applications such as cell separation, magnetic fluid hyperthermia, and contrast agents in the magnetic resonance imaging or drug carriers [1–4].

Several of the synthesis techniques for the preparation of ferrite nanoparticles were applied before, such as co-precipitation, hydrochemical, hydrolysis, sol–gel method [5–8]. The choice of the synthesis method is crucial in order to obtain desired composition, size, magnetic and other properties of the nanoparticles. Moreover, different high-energy ball milling or alloying techniques used for the preparation of ferrite nanomaterials may serve as the way to obtain larger quantities of nanomaterials. Magnetite, maghemite nanosized materials were obtained by milling hematite with iron [9], iron in water [10–12], or hematite in ethanol [13]. The high-energy ball milling was used for the synthesis of ferrite nanoparticles using metal hydroxides or double layered hydroxide carbonates as precursors [14–16] prepared by the usual co-precipitation in the metal salt solution. Using solid metal salts as precursor in the high-energy milling also leads to the formation of the ferrite nanoparticles as it was showed by mechanochemical synthesis of $BaFe_{12}O_{19}$ [17] and magnetite nanoparticles [18]. In this study $CoFe_2O_4$ and $MnFe_2O_4$ nanoparticles were obtained by mechanochemical synthesis using Fe and Co(Mn) salts and investigating the influence of milling conditions on the size and magnetic properties of the nanoparticles.

2. Method

The analytically pure reagents $CoCl_2 \cdot 6H_2O$, $MnSO_4 \cdot H_2O$, $Fe_2Cl_3 \cdot 6H_2O$ and KOH (Eurochemicals) were used to obtain Co and Mn ferrites according to the reaction

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$$Co^{2+}\left(Mn^{2+}\right) + 2 \bullet Fe^{3+} + 8 \bullet OH^{-} \rightarrow Co(Mn)Fe_2O_4 + 4 \bullet H_2O \quad (1)$$

Surplus of cobalt chloride (10%) and potassium hydroxide (100%) required by the reaction were taken to achieve more stoichiometric cobalt ferrite and to ensure stable conditions of the reaction. All reagents, total mass of 63 g, were placed into the 250 ml steel vial together the steel balls, each 5 mm in diameter and 600 g in total mass. 40 g of NaCl was added in the other synthesis experiments. The $CoFe_2O_4$ and $MnFe_2O_4$ nanoparticles were synthesized using Pulverisette 6 high-energy planetary monomill (Fritsch GmbH). The rotational speed and milling time varied between 200 and 400 rpm and 5–30 min, respectively. The synthesized particles were washed with the deionized water, centrifuged several times and stabilized with the citric acid to obtain stable ferrofluids.

Mössbauer spectra were measured using $^{57}Co(Rh)$ source in the transmission geometry. The samples for the Mössbauer studies were prepared by drying ferrofluid onto the shred of the filter paper. The low temperature spectra were obtained by placing the samples into the closed cycle He cryostat (Advanced Research Systems, Inc.). The hyperfine field B distributions and separate sextets or doublets were applied to fit to the Mössbauer spectra using WinNormos (Site, Dist) software when required.

XRD patterns were measured using an X-ray diffractometer SmartLab (Rigaku) equipped with 9 kW rotating Cu ($\lambda = 1.5418$ Å) anode X-ray tube. IDDC data base PDF4+ was applied for the identification of minerals. The nanoparticle (crystallite) sizes D were calculated using Scherrer equation:

$$D = \frac{0.94\lambda}{\beta_{1/2}\cos\theta}, \quad (2)$$

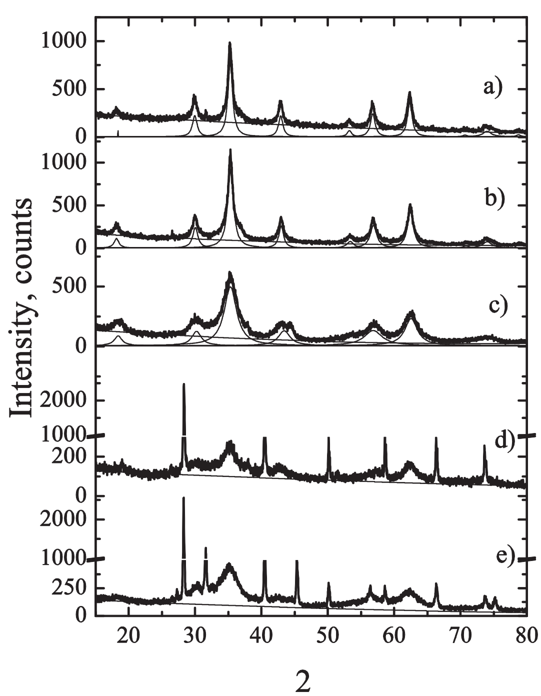

Fig. 1. XRD patterns of (a–d) $CoFe_2O_4$ and (e) $MnFe_2O_4$ nanoparticles powder prepared by mechanochemical synthesis with the addition of NaCl (a,b,e) and without NaCl (c,d) at milling speed 400 rpm (a,c,e) and 200 rpm (b,d). Broad lines are from ferrite nanoparticles, sharp lines are due to KCl and NaCl.

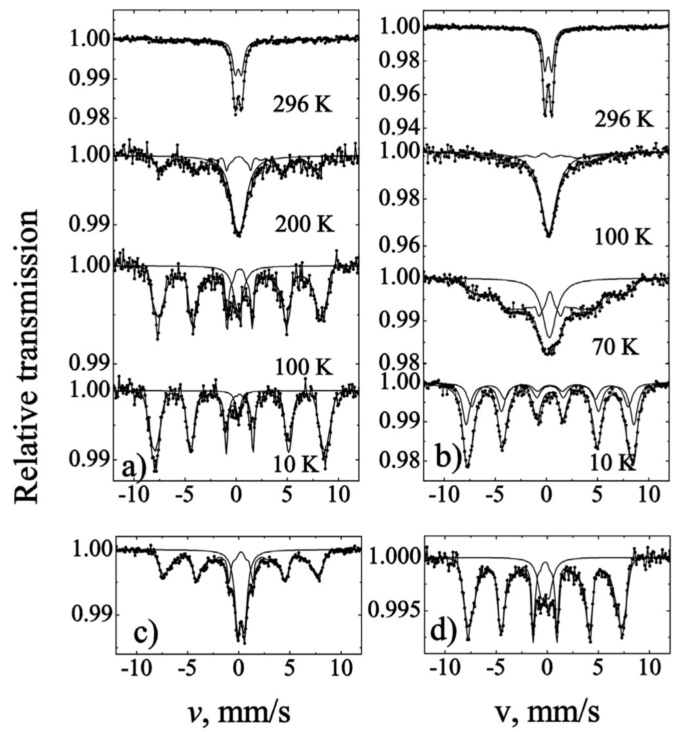

Fig. 2. Mössbauer spectra of (a) $CoFe_2O_4 \approx 4$ nm size nanoparticles synthesized at 400 rpm without addition of NaCl, (b) $MnFe_2O_4$ (≈ 3 nm) nanoparticles synthesized at 400 rpm without addition of NaCl, (c) $CoFe_2O_4$ (≈ 8 nm) nanoparticles synthesized at 200 rpm with addition of NaCl and (d) $CoFe_2O_4$ (≈ 10 nm) nanoparticles synthesized at 400 rpm with addition of NaCl.

where λ is the source wavelength, $\beta_{1/2}$ is the peak full width at half maximum (FWHM) at the diffraction angle θ.

AFM images of the nanoparticles, deposited from the diluted ferrofluid on clean Si substrate, were acquired with the NanoWizard3 atomic force microscope (JPK Instruments AG, Berlin, Germany) in the AC mode, using Tap300Al-G probes (BudgetSensors). The particle size was determined by measuring the nanoparticle height from the 2 × 2 μm^2 or 1 × 1 μm^2 field images. Digital image processing and the height measurements were done with the JPK Data Processing software. The Si substrate surface was equalized to 0 nm in height. Nanoparticle height distribution was

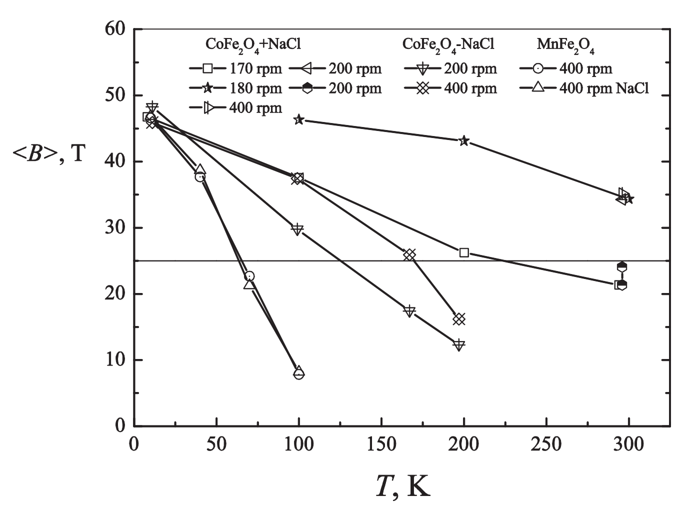

Fig. 3. Dependences of average hyperfine field of Mössbauer spectra of $CoFe_2O_4$ and $MnFe_2O_4$ nanoparticles synthesized at indicated conditions on temperature.