



A detailed study on the transition from the blocked to the superparamagnetic state of reduction-precipitated iron oxide nanoparticles



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ABSTRACT

Magnetic iron oxide nanoparticles were prepared by salt-assisted solid-state chemical precipitation method with alternating fractions of the ferric iron content. The physical properties of the precipitated nanoparticles mainly consisting of magnetite were investigated by means of transmission electron microscopy, high energy X-ray diffraction, vibrating sample magnetometry and Mössbauer spectroscopy. With particle sizes ranging from 16.3 nm to 2.1 nm, a gradual transition from the blocked state to the superparamagnetic state was observed. The transition was described as a dependence of the ferric iron content used during the precipitation. Composition, mean particle size, coercivity, saturation polarisation, as well as hyperfine interaction parameters and their evolution were studied systematically over the whole series of iron oxide nanoparticles.

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1. Introduction

With the reduction of the particle size remarkable physical phenomena are observed. Finite-size effects and particle size distributions, intrinsic properties, as well as the particle interactions become more important [1–3]. Particularly, the interest in magnetic nanoparticles based on iron oxides rose drastically because of their wide range of potential applications, especially in biomedicine [4–8]. The main questions in all applications are how the nanostructure modifies the electric and magnetic properties and how one can take advantage of the nanostructure to improve specific properties for the desired application. Therefore, various methods of synthesis have been developed [9–11]. A relatively new and efficient method is the salt-assisted solid-state chemical precipitation, which stands out because it is organic-solvent free and has no need for a controlled atmosphere [12,13].

Magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) are the most important ferrimagnetic compounds among all iron oxides. The stoichiometry of magnetite, which is often referred to as a solid solution of magnetite and maghemite, strongly influences the

physical and chemical properties like the reduction potential, the coercivity as well as the crystal structure of the particles [14]. Magnetite has a cubic unit cell which belongs to the space group Fd $\bar{3}$ m and it has a crystal unit edge of $a \approx 8.39$ Å [15]. The unit cell of the stoichiometric spinel contains 32 oxygen atoms and has 8 equivalent tetrahedral (A-sites) and 16 equivalent octahedral sites (B-sites) which can be occupied by iron atoms. It is worth to mention that the tetrahedral sites are occupied by trivalent iron and the octahedral sites contain not only trivalent but also divalent iron.

The formula Fe₃O₄ can be written as (Fe³⁺)_{tetra}[Fe³⁺ + Fe²⁺]_{octa}O₄²⁻ [16]. Magnetite has a wide range of oxidation states depending on the structural Fe²⁺ states which can be discussed as the stoichiometry of magnetite ($x = \text{Fe}^{2+}/\text{Fe}^{3+}$). $x=0.5$ corresponds to the stoichiometric magnetite Fe₃O₄ and $x=0$ to its completely oxidised form, maghemite γ-Fe₂O₃. Maghemite has a crystal unit edge of $a \approx 8.33$ Å [15]. For non-stoichiometric magnetite, the structure formula can be written as Fe_{3-δ}O₄ with δ ranging from 0 to 1/3. Assuming that the vacancies □ are only present on the octahedral sites, the formula can be rewritten as (Fe³⁺)_{tetra}[Fe³⁺_{1+2δ} + Fe²⁺_{1-3δ}□]_{octa}O₄²⁻ [14].

⁵⁷Fe Mössbauer spectroscopy creates the possibility to study the stoichiometry of ferrites. Mössbauer spectra contain information about the structure, the electronic and magnetic properties of

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the tested material i.e. relative intensities corresponding to particular phases and three hyperfine interaction parameters: isomer shift (IS), quadrupole splitting (QS) and magnetic hyperfine field ($\mu_0 H_{hf}$). The isomer shift gives information about the electric monopole interaction between protons (nucleus) and atomic electron cloud (mainly s-electrons), which results in different shifts of nuclear levels. The quadrupole splitting describes the electric quadrupole interaction between the nuclear quadrupole moment and electric field gradient at the nucleus. It causes a splitting of the nuclear states into $I+1/2$ substates. The magnetic hyperfine field characterises the magnetic dipole interaction between the nuclear magnetic dipole moment and magnetic field at the nucleus, leading to a splitting of the nuclear states into $2I+1$ substates [17,18]. These three types of hyperfine interactions between the electronic environment and the probed nucleus are conventionally described by a Hamiltonian containing the hyperfine parameters. This Hamiltonian is highly sensitive to changes in the local electronic structure. Therefore, it is sensitive to changes resulting from the particle size reduction.

Since there is a multiple number of different synthesis methods and a wide range of parameters, including the stoichiometry of magnetite, directly influencing the properties of the resulting nanoparticles, a complete picture of the characterisation of magnetic nanoparticles has not been established yet and it opens the possibilities for further systematic studies. Hence a detailed investigation of iron oxide nanoparticles prepared by precipitation method was performed at room temperature. The particle size, as well as the crystallite sizes, the crystal unit edges and the composition have been determined. Moreover, the saturation magnetisation, the coercivity and the hyperfine interaction parameters have been studied in dependence of the ferric iron content used during the synthesis.

2. Experimental details

In order to obtain magnetite nanoparticles with different particle sizes, the salt-assisted solid-state chemical precipitation method was applied [12]. Mixtures of ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) with different ratios were blended in an excess of sodium hydroxide (NaOH) [12]. All the reagents were weighted using a precise laboratory balance and an overview of the used materials for each sample is collected in Table 1. For each sample, the fraction of initially used ferric iron $\zeta = \text{Fe}^{3+} / [\text{Fe}^{3+} + \text{Fe}^{2+}]$ was changed. The iron chlorides and the sodium hydroxide were ground separately for several minutes and afterwards the powders were blended together constantly during the whole reaction. It is worth to mention that during the reaction heat and vapor were released. The mixture was cooled down and washed with water several times until a pH-value of approximately 7 was reached. Eventually, the mixture was dried.

The obtained powders were studied by the transmission electron microscope Libra 120, Carl Zeiss AG in order to observe

Table 1
Overview of the materials used for the synthesis of nanoparticles and the initial ferric iron fraction ζ .

Sample	m_{NaOH} (g)	$m_{\text{FeCl}_2 \cdot 4\text{H}_2\text{O}}$ (g)	$m_{\text{FeCl}_3 \cdot 6\text{H}_2\text{O}}$ (g)	ζ
S1	5	5	0	0
S2	5	4	1	0.16
S3	5	3	2	0.33
S4	5	2	3	0.52
S5	5	1	4	0.75
S6	5	0	5	1.00

changes in the morphology and the particle size.

High energy X-ray diffraction experiments were performed at the High Energy Material Science (HEMS) beamline P07 located at the high brilliance synchrotron radiation storage ring PETRA III, DESY Germany. The basic design parameters of the storage ring are an energy of 6 GeV and a current of 100 mA. The source of X-rays for HEMS was a 2 m long standard PETRA undulator. The investigations were performed in the test facility EH1 using an indirectly water-cooled single bounce monochromator with a Si (220) Laue single-crystal leading to monochromatic synchrotron radiation with a wavelength $\lambda = 0.1424 \text{ \AA}$ [19,20]. The experiments were carried out in Debye-Scherrer geometry with a sample to detector distance of 1194 mm. The diffraction patterns were collected with a Perkin Elmer image plate detector ensuring fast data acquisition.

Vibrating sample magnetometry was applied to determine the hysteresis of the synthesised nanoparticles at room temperature. Each powder was precisely weighted and embedded in paraffin wax. The samples vibrated with a small amplitude in a region of uniform but variable magnetic field. An alternating voltage was induced in the surrounding coils, which was proportional to the magnetisation of the sample.

The ^{57}Fe Mössbauer spectroscopy studies were performed in transmission geometry at room temperature. The γ -ray source was 25 mCi ^{57}Co embedded in a Rh-matrix, mounted on a FAST Comtec Mössbauer drive unit working in constant acceleration mode. Mössbauer transmission spectra were collected with a scintillation counter in a velocity range $\pm 11 \text{ mm/s}$ with 1024 channels before folding. It is worth to mention that a standard α -Fe foil was used for calibration and the isomer shift is given with respect to iron at room temperature.

3. Results

3.1. Transmission electron microscopy

Exemplary images of each sample are presented in Fig. 1. With an increasing amount of ferric iron ζ used during the precipitation a significant decrease of the particle size was observed.

3.2. High energy X-ray diffraction

The diffraction patterns were integrated in 5° steps and each of the obtained spectra was processed applying Rietveld refinement procedure [21] combined with Fourier analysis, as implemented in the MAUD code [22,23]. Fig. 2 shows the experimental and the calculated pattern, as well as the differential pattern. The synthesised powders were composed not only of magnetite but they also contained small amounts of goethite and iron. The resulting composition, the crystal unit edge and the crystallite size of magnetite are collected in Table 2. A significant increase in the line width of the diffractograms with increasing ζ can be observed. With the reduction of the particle size, the diffraction peaks show significant broadening. This makes the interpretation of the diffractogram for the nanoparticles which were precipitated only from ferric chloride hexahydrate, especially challenging.

3.3. Vibrating sample magnetometry

The resulting hysteresis curves are presented in Fig. 3. The coercivity and the saturation polarisation were determined from the obtained hysteresis curves. The coercivity was obtained by fitting a linear function on the left and the right side of the hysteresis and forming the average value. The saturation polarisation was calculated by extrapolating J versus $1/H$ for $1/H \rightarrow 0$.

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