

# Mössbauer characterization of surface-coated magnetic nanoparticles for applications in transformers

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**Abstract** In this study the synthesis of very small magnetite nanoparticles is reported. Analysis of the (311) X-ray diffraction line indicates nanoparticle with 2.2 nm average diameter. The as-synthesized nanosized magnetite sample was submitted to a chemical oxidation process for conversion to maghemite. However, the yielding of the chemical oxidation process, as indicated by the analysis of the Mössbauer data, was about 20%. This finding indicates a strong size-dependence of the oxidation process, reducing the yielding of the chemical process used as the nanoparticle size reduces down to extremely low values.

**Keywords** Mössbauer · Magnetite nanoparticle · Oxidation process · Size-dependence · Magnetic fluid · Transformer

## 1 Introduction

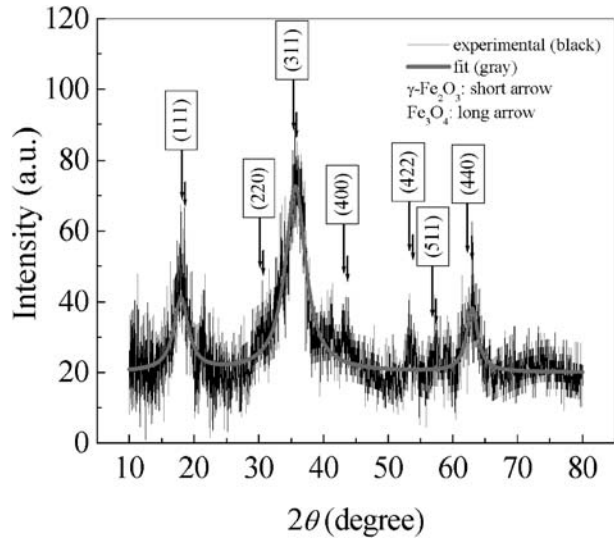
Development of oil-based magnetic fluid (MF) samples for use in high voltage transformers technology requires highly-stable MFs, displaying specific electrical properties and able to operate at temperatures above 100°C and under high voltages for long periods of time [1]. Colloidal stability of organic-based MF samples can be achieved via balancing the Van der Waals, magnetic dipole and steric interactions,

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**Fig. 1** X-ray diffractogram of the sample after the oxidation process. The *gray solid line* is the curve-fitting of the three main features using Lorentzian shaped curves. The standard X-ray lines of magnetite and maghemite are indicated with long and short arrows, respectively



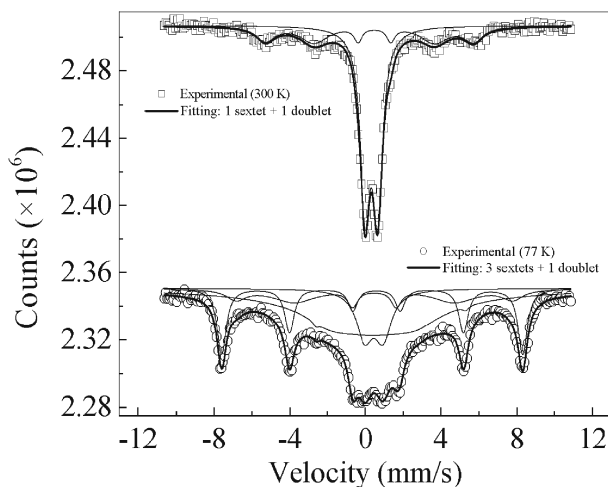
the latter due to the presence of long chain hydrocarbon molecules comprising the molecular shell dressing the suspended magnetic core nanoparticle. Phase stability of the magnetic nanosized core is also a key issue in producing highly-stable MF samples for applications in high voltage transformers. In this study, Mössbauer spectroscopy was used as the main technique in the investigation of nanosized magnetic particles surface-coated with oleic acid (OA). The nanosized magnetic powder used for OA surface-coating was obtained by oxidation of native nanosized magnetite. Nevertheless, the oxidation process aimed to oxidize magnetite ( $\text{Fe}_3\text{O}_4$ ) up to maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) seems to be size-dependent. Therefore, starting with a polydispersed magnetite sample one has the possibility to obtain a partially-oxidized sample, consisting of a mixture of magnetite and maghemite. In order to investigate this aspect of the nanoparticulated powder sample Mössbauer spectra were recorded at 300 and 77 K. X-ray diffraction (XRD) data of the investigated sample will be used to provide information in regard to the average size of the nanoparticulated material and to support the discussion of the Mössbauer data *regarding the material phases*.

## 2 Experimental

Preparation of native maghemite nanoparticle was accomplished in a two-step procedure whereas its surface-coating with oleic acid (OA) was realized in a third step [2]. In the first step under magnetite nanoparticle was precipitated after pouring NaOH aqueous solution under vigorous stirring into an aqueous solution containing both Fe(II) and Fe(III) ions. In the second step the oxidation of the as-produced magnetite was performed by adding HCl aqueous solution to the fresh black sediment (setting the pH at 3.5) and the resulting suspension was heated at  $97^\circ\text{C}$  under stirring, for 3 h, while oxygen was bubbled throughout the aqueous suspension. In the third step pure oleic acid was added under stirring to the previously-oxidized suspension

**Table 1** Standard XRD lines ( $2\theta$ ) of maghemite (JCPDS-ICDD 1346 chart), magnetite (JCPDS-ICDD 9-629 chart) and the approximated values of the XRD lines ( $2\theta$ ) identified in the sample investigated in the present study

Hkl	111	220	311	400	422	511	440
$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> ( $2\theta$ )	18.38	30.24	35.63	43.28	53.73	57.27	62.92
Fe <sub>3</sub> O <sub>4</sub> ( $2\theta$ )	18.27	30.09	35.42	43.05	53.39	56.94	62.51
This study	18.02	30.44	35.66	43.26	53.06	58.34	63.02

**Fig. 2** Three hundred and 77 K Mössbauer spectra of the sample after the oxidation process. *Open squares* and *circles* are experimental data whereas *thin solid lines* represent the sub-spectra obtained from the curve-fitting using combination of sextets and doublets. The *thicker solid line* represents the convolution of the sub-spectra

whereas the pH was set at 6 by adding NH<sub>4</sub>OH aqueous solution. The suspension was stirred for 30 min. At the end of the third step the OA-coated nanoparticles were captured in organic phase which was separated from the aqueous phase by decantation and further washed with ethanol until the excess of free oleic acid was completely removed. The OA-coated nanoparticles were then dried out (powder sample), removing the ethanol for further suspension in insulating mineral oil to produce the stock diluted MF sample (4 g of the OA-coated nanoparticles in 100 mL of insulating oil). The powder sample produced before the surface-coating step (AO-coating) was investigated using XRD and Mössbauer spectroscopy. Data in Fig. 1 represents the XRD pattern of the OA-coated nanosized sample in the  $2\theta$  range of  $10^\circ$  to  $80^\circ$ , showing the typical reflection lines associated to both magnetite and maghemite. Long (short) arrows represent the standard XRD line positions of magnetite (maghemite), as quoted in the JCPDS-ICDD charts (9-629 and 1346 for magnetite and maghemite, respectively) and collected in Table 1. The peak positions observed in the XRD of the sample investigated are also included in Table 1. The 300 and 77 K Mössbauer spectra of the sample are presented in Fig. 2. Symbols in Fig. 2 represent the experimental points, thin solid lines represent the Mössbauer sub-spectra and the thick solid lines are the best curve fitting for the data. The corresponding hyperfine parameters are collected in Table 2.

**Table 2** Mössbauer parameters associated to the 77 K sub-spectrum obtained from the present study and from the magnetite sample reported on [4]

Spectrum component	IS (mm/s)	QS (mm/s)	IS (mm/s)	QS (mm/s)	HF (T)	Area %
Doublet (Fe <sub>3</sub> O <sub>4</sub> ) <sup>a</sup>	0.46	0.97				13.2
Sextet (Fe <sub>3</sub> O <sub>4</sub> ) <sup>a</sup>			0.48	-0.0003	45.4	16.1
Sextet (Fe <sub>3</sub> O <sub>4</sub> ) <sup>a</sup>			0.89	1.86	24.5	50.2
Sextet ( $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> ) <sup>a</sup>			0.47	-0.23	49.4	20.5
Sextet (Fe <sub>3</sub> O <sub>4</sub> ) <sup>b</sup>			0.40	0.00	50.7	42
Sextet (Fe <sub>3</sub> O <sub>4</sub> ) <sup>b</sup>			0.54	-0.04	52.8	14
Sextet (Fe <sub>3</sub> O <sub>4</sub> ) <sup>b</sup>			0.78	-0.03	49.9	25
Sextet (Fe <sub>3</sub> O <sub>4</sub> ) <sup>b</sup>			0.86	0.02	46.0	15
Sextet (Fe <sub>3</sub> O <sub>4</sub> ) <sup>b</sup>			1.15	2.19	34.5	4

<sup>a</sup>Present study<sup>b</sup>[4]

### 3 Data analysis

Though the XRD data presented in Fig. 1 does not allow the estimation of the magnetite-to-maghemite content ratio precisely it was used for both identifying the XRD peaks associated with the two main phases (magnetite and maghemite) as well as to estimate the average nanoparticle diameter (2.2 nm), the later using the Scherrer's relation [3]. The standard XRD lines associated to magnetite and maghemite (see Table 1) are indicated in Fig. 1 by long and short arrows, respectively. The XRD features observed in Fig. 1 can be quickly identified with the typical XRD lines of magnetite and maghemite, indicating the presence of both phases. The solid gray line in Fig. 1 represents the best curve fitting of the three main XRD features, namely (111), (311) and (440) using Lorentzian lines. The corrected linewidth at half-height of the (311) reflection was used to estimate the average nanoparticle diameter of about 2.2 nm. Analysis of the Mössbauer spectra, however, was used to provide the information in regard to the magnetite-to-maghemite content ratio. The room-temperature Mössbauer spectrum was curve-fitted using one sextet and one doublet, as shown in Fig. 2 (upper panel). Differently, the liquid-nitrogen Mössbauer spectrum was curve-fitted using three sextets and one doublet, as indicated in Fig. 2 (lower panel). Table 2 summarizes the hyperfine parameters obtained from the 77 K Mössbauer sub-spectra. Included in Table 2 are typical hyperfine parameters obtained from the analysis of a nanosized magnetite sample at 77 K, whose Mössbauer spectrum was curve-fitted using five sextets [4].

The Mössbauer spectra presented in Fig. 2, including the spectrum evolution from 77 to 300 K, is typical of superparamagnetic particles [5, 6]. The values we found for the hyperfine parameters of the sub-spectra indicate a mixture of magnetite and maghemite. From the Mössbauer analysis about 20% of the sample is composed by nanosized maghemite whereas about 80% consists of nanosized magnetite, as indicated in Table 2. This assumption is supported by the analysis of the 77 K Mössbauer spectrum as follows. As presented in Table 2 the hyperfine parameters obtained from the analysis of the sextet, here claimed to be associated to nanosized maghemite, is in agreement with the literature [7]. Likewise, the hyperfine parameters obtained from the analysis of the two sextets, here claimed to be associated to nanosized magnetite (sites A and B), is in agreement with the

literature [4, 8]. In addition, the hyperfine parameters obtained from the analysis of the doublet of the 77 K Mössbauer spectrum, here claimed to be associated to nanosized magnetite, is in good agreement with the literature [9]. This conclusion is supported by the XRD features observed in Fig. 1 and quoted in Table 1. As far as the two-phase composition of the sample is concerned the analysis of the Mössbauer spectrum performed at 77 K is consistent with the analysis of the XRD data. Indeed, Mössbauer parameters obtained from measurements performed on nanosized oxide-based magnetic particles, as for instance magnetite, may reveal a significant variability which could be explained by the preparation route employed, including oxidation/reduction steps, average size, size dispersion, and surface functionalization [4].

What is quite surprising from the analysis of the 77 K Mössbauer spectrum is the high content of magnetite, despite the oxidation chemical process the sample was submitted to. This finding indicates the strong dependence of the chemical oxidation yielding upon the particle size, for this particular oxidation route of magnetite. Our findings indicate that the oxidation yielding reduces as the average magnetite nanoparticle size reduces. The literature reports high oxidation yielding of magnetite using this chemical route, but the average particle diameter used by van Ewijk et al. [2] was about 10 nm. In addition, as far as the particle size dispersion is concerned the literature reports wide distributions [2]. This characteristic supports the hypothesis of partial oxidation of magnetite to maghemite, taking place only in the higher particle size end of the size distribution. We then hypothesize that the oxidation process possibly creates a selective (size-dependent) fraction of core-magnetite structure, extremely small, responsible for the doublet observed at 77 K. Within this picture the oxidized sample may be best represented by a bimodal distribution of nanosized magnetite, the bigger component being responsible for the sextets observed at 77 K. Note that the (311) X-ray linewidth may probe the smallest component of this bimodal distribution with an average diameter of 2.2 nm. Actually, further analysis taking into account samples with quite different average particle diameter is presently under progress to elucidate the size-dependence of the chemical oxidation route used in this study.

## 4 Conclusions

In conclusion, nanosized magnetite particles was synthesized and further oxidized to maghemite. However, the oxidation chemical route used in the present study seems to be strongly size-dependent. In the very small size limit the oxidation process used here presented a reduced chemical yielding, as indicated by the analysis of the Mössbauer spectra. These findings were also supported by X-ray diffraction analysis.

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