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Original Research Paper

# Influence of process control agent type on the mechanosynthesis of $Fe_3O_4$ particles

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ABSTRACT

The influence of the nature of the process control agent (PCA) used in the mechanosynthesis of the magnetite nanoparticles has been studied. The two-step route used here for obtaining nanocrystalline/-nanoparticles $Fe_3O_4$ consists of a heat treatment, to prepare well-crystallised magnetite, followed by the mechanosynthesis process. Dry milled magnetite samples have been obtained as a reference, using the same conditions (duration and energy), to determine the influence of the process control agents (PCA). Three different PCAs have been used: benzene, ethanol and oleic acid. The characterisation of the magnetite particles has been performed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), magnetic measurements M(H), differential scanning calorimetry (DSC) and thermogravimetric (TG) measurements and Scanning Electron Microscopy (SEM). XRD and SEM analysis revealed a different processing mechanism for the two milling modes, wet and dry. In the case of dry milling, even for short milling times, iron contamination and formation of a wüstite – FeO phase is noticed. The use of the PCA during the milling process limits the above-mentioned contamination. Ethanol and benzene uses as PCA lead to synthesis of fine uniform sized particles. SEM images reveal the presence on nanoparticles. In the case of oleic acid, DSC, TG and magnetic measurements revealed the presence of a thin layer of oleic acid adsorbed on the particles. FTIR analysis highlighted the presence of both free and bonded oleic acid. The magnetisation of the samples was found to be linked to the powder contamination (FeO or oleic acid), structural defects or finite size effects.



## 1. Introduction

Soft magnetic ferrites represent an important and large class of magnetic materials, mainly due to their interesting electrical and magnetic properties [1–5]. These properties originate from their cubic spinel structure (space group Fd-3m), named after the spinel ($MgAl_2O_4$) mineral [1,3]. Due to their ceramic nature, the spinel ferrites present high electrical resistivity [1,2]. The combination of their high electrical resistivity and magnetic properties makes the soft magnetic ferrites usually well suited for mid and high-frequency applications, where metals and alloys are limited. The electrical resistivity of the spinel ferrites ($MeFe_2O_4$) varies from $10^{-3}$ Ω·cm (Me═Fe) up to $10^{7}$ Ω·cm (Me═Mg) depending on the type of metallic cation [3]. The magnetisation of the ferrites is given by the distribution of the divalent and trivalent metallic ions in octahedral (B) and tetrahedral (A) sites [3]. In the case of iron ferrite (ferrous ferric oxide), also known as magnetite, the $Fe^{3+}$ ions are distributed equally in the two sites, while the $Fe^{2+}$ ions are distributed in the B sites. Although iron ferrite reveals low electrical resistivity compared to the other spinel ferrite, its magnetic moment is among the highest, presenting thus high interest. In the past years, by monitoring the size and structure of the particles, the domain of potential applications of the magnetite has grown significantly since nanoparticles of $Fe_3O_4$ exhibit new characteristics dissimilar to the bulk samples [4,5]. The potential applications of the nanosized ferrites are numerous, such as medical applications: drug delivery systems, magnetic hyperthermia, magnetic resonance imaging, separation of cells [6,7], electronics: high-density data storage, sensor technology, antenna miniaturisation [8,9], and even for spintronic [10,11] or magnetocaloric refrigeration [11].

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Several synthesis techniques can be used for obtaining iron ferrite: sol-gel [12], co-precipitation [7,13,14], ceramic method [1–3], mechanosynthesis [6,8,15,16] or microemulsion [17]. Mechanosynthesis is a versatile and well-suited technique to prepare magnetite nanoparticles and for controlling the size of particles and crystallites, starting from different precursors [6,8,15,16]. For instance, R. Kumar et al. [6] have reported the obtaining of magnetite from mineral waste, containing $Fe_2O_3$, $SiO_2$ and $Al_2O_3$, by a combined method (mechanosynthesis and chemical route). In the first step, the iron ore was milled with complementary iron for the reaction of hematite.

In Ref. [8] is presented the mechanosynthesis of $Fe_3O_4$, starting from elemental iron. By using distilled water as PCA, the influence of milling time on the synthesis of $Fe_3O_4$ has been studied. The complete formation of $Fe_3O_4$ by this method occurs only after 48 h of milling. The as obtained magnetite has the mean crystallite size of about 30 nm. The magnetisation of the samples revealed a decrease upon increasing milling time, due to the continuous formation of magnetite from elemental iron and to the surface effects characteristic of small particles.

According to Refs. [15,16], under certain milling conditions (in either air or oxygen atmosphere), the mechanosynthesis of hematite, $\alpha$-$Fe_2O_3$, is leading to the formation of $Fe_3O_4$. The phase's transformations have been observed to be linked to the oxygen partial pressure. Processing in dry oxygen leads to a slower reaction rate as compared to air. For prolonged milling duration, the authors observed the formation of the FeO phase.

The classical ceramic method is divided into several steps, such as homogenization of the precursor powder, followed by compaction and finally heating up to temperatures above 1200 °C. The development of more efficient and simpler processing techniques that ensure the solid state reaction is a significant part of the soft magnetic ferrite research. In this study, we have synthesised the magnetite particles by a combined two-step route. First, a pseudo-ceramic method, consisting in the homogenisation and then heating to temperatures about 50% lower than the classical one. In the second step, the as obtained magnetite powder was subjected to wet mechanical milling using three types of process control agents: oleic acid, ethyl alcohol and benzene. One of the main upsides of the wet milling is the ability to control the particle or crystallite size in the mechanosynthesis process. In this article, we focus our attention on the influence of the PCA nature on the structural, thermal and magnetic characteristics of $Fe_3O_4$ milled powder.

## 2. Materials and methods

High purity Fe (>99.5%) and $\alpha$-$Fe_2O_3$ (>98%) powders have been homogenised and heat treated as described in [18]. The as-obtained powder has been processed in a Fritsch Pulverisette 6 planetary ball mill, using both dry and wet milling technique. Three types of PCA have been used: benzene – $C_6H_6$, ethanol – $C_2H_6O$ and oleic acid – $C_{18}H_{34}O$. The amount of used PCA was chosen in respect to the following powder to PCA mass ratio of 50/1. The rotational speed of the disc was set at 350 rpm. The used transmission ratio of the planetary disk/grinding bowl is $i_{relative} = 1:-1.82$. Tempered steel milling balls (83 balls, $m_{ball} = 12g$, 12 mm diameter) and vial ($V_{vial} = 500$ ml) were preferred. The ball to powder mass ratio – BPR was chosen to be 20:1, which led to a filling factor of about 60%. The centrifugal acceleration developed by the mill in the current setup is about 29g ($g = 9.81\ m/s^2$). To avoid powder oxidation, during sampling after certain milling times, both powder milling and powder handling were done an argon atmosphere.

The as-milled samples were characterised by X-ray diffraction (XRD) using $CoK_\alpha$ radiation ($\lambda = 1.7903$ Å) from an INEL EQUINOX 3000 diffractometer. Deriving from the XRD measurements, the mean crystallite size and the lattice strain were calculated with the Williamson-Hall method [19]. The full width at half maximum (FWHM) of the five most intense peaks of iron ferrite ((2 2 0), (3 1 1), (4 0 0), (5 1 1), (4 4 0)) has been determined using the Fullprof software. The instrumental broadening has been determined from the line broadening of a standard, well-crystallised sample. Next, after subtracting the instrumental broadening, the FWHM of the peak is given by the crystallite size ($\beta_D$) and the microstrain ($\beta_\varepsilon$) [19]:

$$\beta = \beta_D + \beta_\varepsilon \tag{1}$$

$$\beta_D = \frac{k \cdot \lambda}{D \cdot \cos\theta} \tag{2}$$

$$\beta_\varepsilon = 4 \cdot \varepsilon \cdot \tan\theta \tag{3}$$

$$\beta = \frac{k \cdot \lambda}{D \cdot \cos} + 4 \cdot \varepsilon \cdot \tan\theta \tag{4}$$

To separate the strain component from the size component Eq. (4) can be rearranged, leading to the following formula:

$$\beta \cdot \cos = \frac{k \cdot \lambda}{D} + 4 \cdot \varepsilon \cdot \sin\theta \tag{5}$$

By plotting $\beta \cdot \cos\Theta$ versus $4 \cdot \sin\Theta$, one can determine the mean crystallite size – D and the strain component – $\varepsilon$ (lattice strain) from the intercept and the slope respectively.

The amount of disordered phase ($F_{GB}$), situated at the grain boundary, was calculated using the following formula [20]:

$$F_{GB} = \left(1 - \left(\frac{D-\Delta}{D}\right)^3\right) \cdot 100 \tag{6}$$

where D represents the mean crystallite size, calculated by the Williamson-Hall method, and $\Delta$ represents the effective thickness of the disordered phase/grain boundary, which was considered of 2–3 atomic layers.

The influence of the PCA on the morphology of the samples, as well as on the particles size and powder homogenisation has been highlighted by field emission scanning electron microscopy (FE-SEM) using secondary electron and in-lens signals by a Sigma Gemini Zeiss Microscope.

Differential scanning calorimetry (DSC) curves have been recorded with a Setaram Labsys DSC/TG apparatus. The samples have been heated up to 900 °C in argon flux, to observe any phenomenon which may occur either when heating or cooling from 900 °C. High purity alumina has been used as a reference, and the heating/cooling rate was 20 °C/min. Also, using the thermogravimetry module from the same apparatus, the mass loss has been recorded when heating under $H_2$ atmosphere up to 300 °C.

The Fourier transform infrared absorption spectra of the samples were obtained using a Jasco FTIR 6200 spectrometer. Before the investigations, the samples were crushed and ground in an agate mortar together with KBr. The as obtained mixture has been compacted and the obtained pellets were used to perform the measurements. All the measurements were done using the same KBr/sample weight ratio 300:2.

The first magnetisation curves have been recorded at room temperature using the sample extraction method in a continuous magnetic field up to 8 T. Both saturation and spontaneous magnetisation have been calculated from first magnetisation curves: saturation magnetization was calculated from the derived $M = f(1/H^2)$ curve and spontaneous magnetisation by extrapolation

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