Seventh International Latin-American Conference on Powder Technology (PTECH 2009)
08 to 10 Nov – Atibaia – São Paulo - Brazil

Synthesis of Magnetite Nanoparticles by Microwave Irradiation and Characterization

Helber Holland [a] and Mitiko Yamaura [b]

Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN-SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP - Brazil
[a] helberholland@hotmail.com, [b] myamaura@ipen.br

Keywords: magnetite nanoparticles, superparamagnetic behavior, characterization, microwave irradiation.

Abstract. Nanometer-scale magnetic particles have been research target because of their peculiar magnetic properties as observed in magnetite nanoparticles. These nanoparticles exhibit superparamagnetic characteristics with potential applications in biomedical, environmental, and engineering fields. In this work, magnetite nanoparticles from Fe^{2+} ions were obtained from two different processes, by precipitation and heating in a boiling water bath and by precipitation and heating in a domestic microwave oven. Influence of heating time of both systems for obtaining of magnetite particles was investigated. The characterization of the products was done by Scanning Electron Microscopy to determine the morphology, X-ray Diffractometry to estimate the crystal structure and the size of crystallite and Fourier Transform Infrared Spectroscopy to show the principal bands of absorption.

Introduction

During the past years, nanoparticles research has become the focus of intense activity, and the synthesis and characterization of nanoparticles have attracted considerable attention from both fundamental and applied research because of their unique optical, electrical, and other properties [1].

The unique phenomena that nanomaterials exhibit are dependent not only on the chemical constituents, but also on the size and shape of the nanomaterial. It is known that the rate control of nucleation is the key to control the size, shape and homogeneity of the nanomaterials. One approach to obtaining this control is the use of microwave systems in synthesis. Besides the advantage of reducing reaction times from days to minutes, the nucleation processes are better controlled under microwave conditions since the reaction is driven by the quick heat and pressure produced by the microwave system. An added advantage is that the amounts of reactants and solvents used in the synthesis are reduced [2].

Magnetite. It is an oxide formed by iron ions of valences 2+ and 3+. It has a cubic crystal structure of the spinel type [3] which oxygen ions form a face-centered cubic arrangement [4]. The spaces between the cubic network structure is occupy by smaller metal ions, and these spaces are of two different kinds, one called tetrahedral e other called octahedral, depending of oxygen ions position. Due the oxygen electronegativity, the normal spinel structure can be inverted, such as the magnetite structure classified as a cubic ferrite with inverse spinel structure.

Structurally, it is represented by $[Fe^{3+}]\{Fe^{2+}Fe^{3+}\}O_4$, where [ ] denotes cations on tetrahedrons sites and { } in the octahedral [5].

Magnetite has in the chemical composition 31.0% of FeO and 69.0% of Fe_2O_3, density of 5.2 g.mL^{-1}, hardness 5.5 to 6 and its melting point is 1597 °C. It is a compound soluble in acid and insoluble in water. It is found in nature as octahedron crystals of black color. It is an iron ore known as a natural magnet found in deposits of iron and one of the most used for obtaining iron and steel [6].

In the presence of a low external magnetic field, the powder consisting of nanoparticles of magnetite tends to orient itself with high saturation magnetization by the magnetic field. With the distance of the magnetic field, the powder loses its magnetization acquired. This property is characteristic of superparamagnetic materials.

Due to the simple crystal structure, magnetite powder can be easily prepared in laboratory. In literature are reported several methods of synthesis of magnetite, such as by microemulsion, sol-gel process, alkaline hydrolysis of ferrous sulphate solution, followed by heating at 100°C, reduction of hematite and others. These methods allow the synthesis of magnetite in various sizes and furthermore, spend much time and material to obtain the final product, which are crucial issues.

Alternative technological methods need to be developed to simplify existing ones or to improve on present methods. An alternative is microwave irradiation because it is easily generated.

Recent studies show that microwave synthesis implies a fast, simple and efficient method to prepare nanometer particles [2]. It has been found that in many cases reaction times can be reduced, in contrast to classical synthetic approaches, and the formation of undesired byproducts can be suppressed [3]. Microwave irradiation as an efficient heating method has been widely used in chemistry since 1986 [7].

Compared with the conventional methods, the microwave synthesis has the advantages of rapid growth, small particle size and narrow particle size distribution due to fast homogenous nucleation [8].

Microwave Irradiation. In a domestic microwave oven, microwaves are produced by an electronic valve called magnetron, which emit microwave on 2.45 GHz frequency. These waves reflect in the walls of the oven and hit the substance placed inside it on many angles. The waves pass through glass and plastic without appreciable effect. However, they have considerable effects on polar molecules: a polar molecule turns, trying to align itself with the electromagnetic wave. The friction between molecules produces heat.

For this phenomenon, submitting samples to microwave besides reducing reaction time, fewer materials are needed. In addition, the use of microwave promotes the controlling of reaction processes.

The closer to the spherical form and more uniformity between the forms, greater will be the efficiency of nanoparticles with bigger applicability, either as ferrofluid, as separating of cells or removal of pollutants [9].

In this present work, the objective is to demonstrate simple and rapid methods for producing magnetite nanoparticles. Influence of heating time in preparation of magnetite nanoparticles by microwave radiation using a domestic microwave oven and water bath was investigated, and their characterization by Scanning Electron Microscopy, X-ray Diffractometry and Fourier Transform Infrared Spectroscopy was done.

Experimental Procedure

Materials.

- Semi-analytical balance QUIMIS MOD Q-500L210C;
- Microwave Consul Facilite, MOD CMS25ABHNA, Potency 700W, Frequency 2450 MHz;
- pHmeter Metrohn Herison MOD E512;
- Pipettes Eppendorf-Research MOD 2055656;
- Fe^{2+} Sulphate heptahydrate Merck COD TA 988065133;
- Sodium HydroxideVetec COD 0705986;
- Acetone (C_2H_6O) Merck;
- Mercury Thermometer MOD 21110-00;
- Glass Laboratory (becker, glass rods, balloons, glass clock etc).

Preparation of Magnetite Nanoparticles no Heating. Magnetite nanoparticles were prepared by the precipitation method. Sample of 1.81 g of $FeSO_4.7H_2O$ (Iron sulfate heptahydrate) was dissolved in 100 mL of distilled water. Then the system was brought to the homogenizer (6000-10000 rpm) and in order to obtain the precipitate of iron oxide and oxyhydroxide 2 $mol.L^{-1}$ NaOH (sodium hydroxide) was slowly added until to reach pH 11. After remaining of the precipitate in solution for 24 h, the system was placed on a magnet for 2 min, so the supernatant was discarded. The separated precipitate was washed several times with distilled water, and was dried at room temperature (25 °C).

Preparation of Magnetite Nanoparticles with Water Bath Heating. Magnetite nanoparticles were prepared from a solution containing Fe^{2+} ions as described above. Subsequently, the system was placed in water bath at 98°C instead of repose for 24 h, to complete the reaction of precipitate formation. Two times of heating, 10 and 30 min were studied. After that, the system was placed on a magnet for 2 min, the supernatant was discarded and the precipitate separated and washed several times with distilled water. The last washing was carried out with acetone and the precipitate was left to dry.

Preparation of Magnetite Nanoparticles with Microwave Irradiation Heating. The same procedure for preparing precipitate was used, however replacing the step of water bath heating by microwave irradiation. We used microwave irradiation (280 W, 2450 MHz) under ambient pressure. Heating times of 1 and 10 min were studied. After that, the precipitate was removed from the supernatant by the magnetic separation technique, was washed several times and left to dry.

Characterization Techniques

Scanning Electron Microscopy. The morphological and structural features were recorded in a Scanning Electron Microscope Philips model XL-30. Samples were put on a metallic support, and covered with gold to obtain the appropriate resolution and contrast.

X-ray Diffractometry. The sizes of magnetite nanoparticles were investigated by X-ray Diffractometry, which was recorded by using a Rigaku Diffractometry model Miniflex II using CuKα (30 kV and 15 mA) radiation.

The average sizes of magnetite crystals were calculated using the equation of Scherrer [10], applied to the measure of the width from the half height of the peaks of diffraction of plan (hkl) 311:

$$D_{rx} = \frac{0.89\lambda}{\Delta\theta \cos\theta} \qquad (1)$$

Where: λ is the wavelength (1.5406 $\overset{\circ}{A}$) of CuK_α radiation, $\Delta\theta$ is the width from the half height, θ is the Bragg angle and 0.89 is a constant related approximately to the shape of magnetite crystallite.

Infrared Spectroscopy. The bands of absorption were identified by Fourier Transform Infrared Spectroscopy using an absorption spectrometer; model BOMEN MB100 with Fourier Transform. Samples were prepared using KBr for dispersion and the spectra were recorded in the range of 4000 cm^{-1} – 350 cm^{-1}.

Results and Discussion

It is known that magnetite has a black color and maghemite has a brown coloration [11]. The maghemite is considered a byproduct of the reaction of Fe^{2+} ions with NaOH. In such a way, it is observed that the final precipitate will have determined coloration by the ratio of each phase, magnetite and maghemite. The color is strongly dependent on the amount of phases of the precipitates. Thus, the final product will have an intermediate color between black and brown color. When the amount of maghemite increases, the final product tends to a brown tonality.

During the precipitate obtaining, the solution of Fe^{2+} ions, initially whitish, turned to a green color and afterwards to a dark-green color with successive additions of NaOH because of the combination of both precipitated iron oxide and iron (II) oxyhydroxide (green) particles. After remaining in solution for 24 h, the precipitate turned to a black color. The precipitates from the heating in water bath and microwave irradiation turned to a black color also. So, based only in the black color, all precipitates resulted in magnetite formation independent of the heating or no of the reaction system. In Fig.1 can be seen the black powder of the magnetite obtained from no heating and its superparamagnetic behavior when it exposed in magnet field of a magnet.

Figure 1. Magnetite powder obtained from the reaction of Fe^{2+} ions and OH^- ions, exposed in magnet field of a magnet.

Scanning Electron Microscopy (SEM). In order to obtain direct information of the particle size and morphology of the magnetite powder, a SEM micrograph was done. Fig. 2 shows the dry particles of magnetite from the no heating reaction system. It was observed that each dry particle is formed by agglomeration of smaller particles of spherical shape. The no regular shape of dry particles is dependent of the amount of agglomerates of smaller particles. This behavior can be attributed to high surface energy of the smaller particles that attract other particles to form grains of particles.

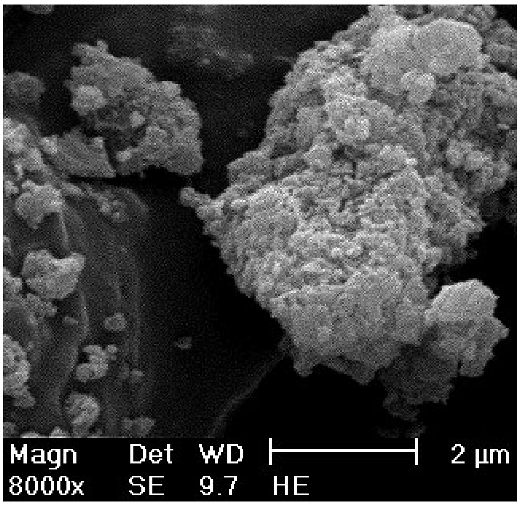

Figure 2. Particle of magnetite obtained from the reaction of Fe^{2+} ions and OH^- ions inside no heating reaction system. Magnitude of 8000x.

Diffraction (XRD). Analysis of XRD spectra was done to confirm the existence of the magnetite and to identify the presence of other phases in samples.

Table 1 shows X-ray diffraction patterns of the possible phases present in the samples, the magnetite phase and maghemite phase. Although these phases have different colors, the crystal structure of face-centered cubic of maghemite (γ-Fe_2O_3) is very similar to that of magnetite (Fe_3O_4). Because of that, the diffraction peaks from magnetite nearly overlap with those from maghemite as can be seen in Table 1. Fig. 3 shows a comparison between the X-ray diffractograms of the samples and patterns of the magnetite and maghemite phases. In general, when magnetite and maghemite coexist together in same samples, it is difficult to identify them by using powder XRD analysis alone.

The spectra in Fig.3 are consistent with the structure of face-centered cubic of magnetite and it was the phase predominant in all samples obtained. Other phases like iron oxyhydroxide, hematite, iron sulfate or goethite were not found.

Table 1. Values 2θ and correspondent intensity of the principal XRD peaks of the X-ray diffraction pattern of magnetite phase (JCPDS-ICDD 19-629) and maghemite (JCPDS-ICDD 39-1346).

$FeFe_2O_4$ (Magnetite) JCPDS-ICDD 19-629	Intensity Peak (Magnetite)	Fe_2O_3 (Maghemite) JCPDS-ICDD 39-1346	Intensity Peak (Maghemite)
18.269	8	18.384	4
30.095	30	30.241	35
35.422	100	35.630	100
37.052	8	37.249	3
43.052	20	43.284	16
53.391	10	53.733	10
56.942	30	57.271	24
62.515	40	62.925	34
70.924	4	71.376	3
73.948	10	74.471	5
74.960	4	75.442	2
78.929	2		
86.702	4		

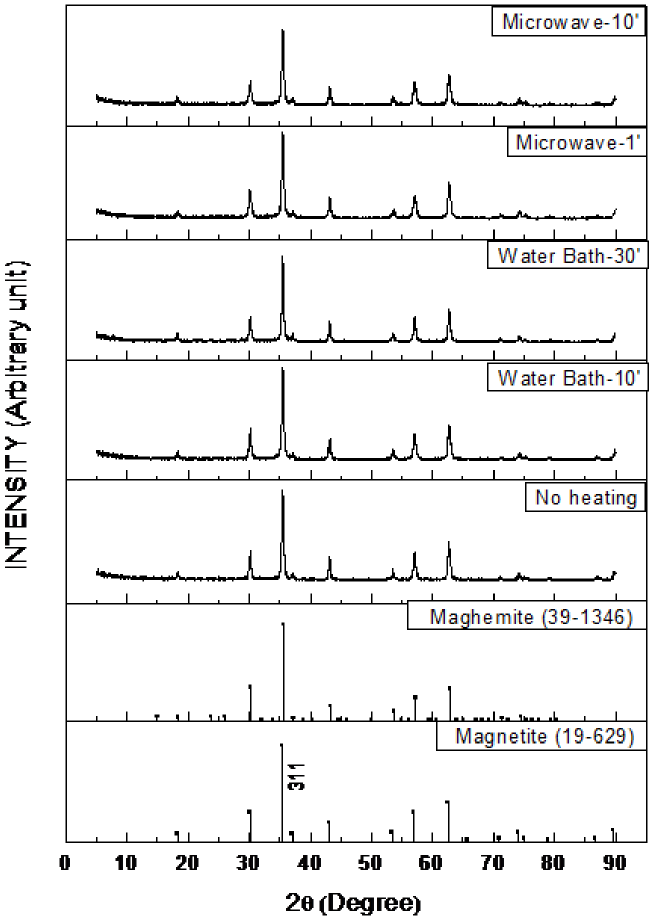

Figure 3. XRD spectra of the magnetite samples and of the patterns of magnetite phase (JCPDS-ICDD 19-629) and maghemite (JCPDS-ICDD 39-1346).

Crystallite size of the magnetite particles was estimated using the Eq. 1 applied to the plan 311. The results are shown in Table 2.

Table 2. Crystallite size of magnetite particles obtained by different methods.

Method	Time of Heating (min)	Size (nm)
Unheated	-	17.2
Water bath	10	17.7
Water bath	30	21.5
Microwave	1	15.7
Microwave	10	17.2

Independent of heating method, with the increase of the heating time it was observed an increase in the crystallite size by nucleation effect. Lower crystallite size was found from the heating of 1 min by microwave irradiation. Crystallite size of 17.2 nm was found for particles obtained unheated and heating by microwave irradiation for 10 min.

Infrared Spectroscopy. The absorption spectra in the infrared region, presented in Fig. 4, showed a strong absorption band at 583 cm^{-1}, which can be attributed to Fe-O/Fe-O-Fe bindings, indicating the presence of magnetite in all samples.
The large band in the region of 3436 cm^{-1} was attributed to νO-H of water of hydration and crystallization νO-H hydroxyl linked to metals. The band at 1632 cm^{-1} was attributed to the angular deformation of water δH-OH [12], in general, associated to water of hydration.

The absorption bands observed in the region of 1132 cm^{-1} can be attributed to the formation of hydroxo complexes (-FeOH/-Fe-OH-Fe)-) similar to those of the metal hydroxides [13]. The hydroxo complexes of magnetite were observed in samples obtained from the reaction system no heating, in water bath for 10 min and by microwave irradiation for 1 min as shown Fig. 4.

The samples heated for longer time as from the reaction system in water bath for 30 min and by microwave irradiation for 10 min not showed bands in the range corresponding to the hydroxo complexes. This suggests a higher perfection and organization of crystal structure lattice of the magnetite nanoparticles in these samples.

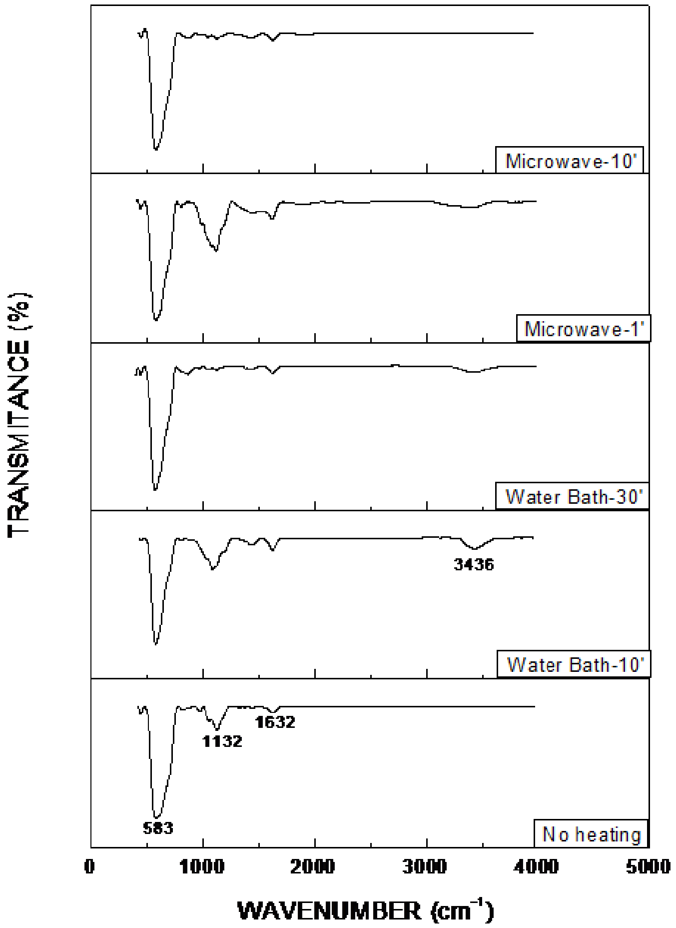

Figure 4. FTIR absorption spectra from the magnetite nanoparticles samples.

Conclusion

In this work, it was presented a comparative study by characterization between the samples of magnetite synthesized from Fe^{2+} ions by microwave irradiation and water bath heating.

The increasing of reaction time of two heating system increased the size of crystallite of nanoparticles and eliminated the hydroxo complexes from crystal structure lattice. Ten minutes of microwave irradiation produced size crystallite of 17 nm and a lattice with no hydroxo complexes. A similar lattice was obtained by water bath for 30 min, however a size crystal of 25 nm. Microwave irradiation reduces the reaction time so that we obtained a crystal with no hydroxo complexes with smaller size in the lower time.

So, these magnetite nanoparticles allow multiple applications in various technological fields.

The synthesis of magnetite nanoparticles using the microwave irradiation proved to be an alternative to the water bath heating producing magnetite nanoparticles of smaller sizes with no hydroxo complexes as impurities.

Acknowledgments

The support of Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and of Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Brazil, is gratefully acknowledged.

References

[1] S. Xuping, L. Yonglan: Size-Controlled Synthesis of Dendrimer-Protected Gold Nanoparticles by Microwave Radiation, Materials Letters Vol. 59 (2005) p. 4048-4050.

[2] J. A. Heuser, W. U. Spendel, A. N. Pisarenko, C. Yu, M. J. Pechan, G. E. Pacey: Formation of Surface Magnetite Nanoparticles from Iron-exchanged Zeolite Using Microwave Radiation, J. Mater. Sci. Vol. 42 (2007) 429057–9062

[3] H. Y. Xua, H. Wanga, Y.Q. Mengb, H. Yana: Rapid Synthesis of Size-controllable YVO4 Nanoparticles by Microwave Irradiation, Solid State Communications Vol. 130 (2004) p. 465-468.

[4] B. D. Cullity in: *Introduction to Magnetic Materials*, John Wiley & Sons, Inc., Hoboken, New Jersey (2009) p. 190-195.

[5] Information on http://www.cq.ufam.edu.br/moleculas/magnetita/magnetita.html. Access on: 08/17/2009.

[6] R. Leal in: *Estudo da Magnetita como Material Adsorvedor de Íons Uranil*, Instituto de Pesquisas Tecnológicas - IPEN, São Paulo, SP (2006) p. 6-7.

[7] M. Faraday, Philos. Trans. R. Soc. Lond, Ser. A Vol. 147 (1857) p. 145.

[8] J. C. Jansen, A. Arafat, A.K. Barakat, H. Van Bekkum, in: M.L. Occelli, H. Robson (Eds.), Synthesis of Microporous Materials, volume 1, Van Nostrand Reinhold (1992) p. 507.

[9] T. G. Diegues, M.C. F.C. Felinto, R.L.Camilo, M. Yamaura, L.C. Sampaio, G.E.S. Brito: Síntese e Caracterização de Nanopartículas Magnéticas de Ferrita de Manganês Dopadas com Eu^{3+} - 17º CBECIMat - Congresso Brasileiro de Engenharia e Ciência dos Materiais, 15 a 19 de Novembro de 2006, Foz do Iguaçu, PR, Brasil

[10] B. D. Cullity in: *Elements of X-ray Diffraction*, Addison-Wesley Publishing Company (1972) p. 99.

[11] Information on http://www.reade.com/eastern-region-(usa)/5257-Maghemite. Access on: 08/22/2009.

[12] R. L Camilo in: *Síntese e Caracterização de Nanopartículas Magnéticasde Ferrita de Cobalto Recorta por 3-Aminopropiltrietoxissilano Para uso como Material Híbrido em Nanotecnologia*, Instituto de Pesquisas Tecnológicas - IPEN, São Paulo, SP (2006) p. 105.

[13] K. Nakamoto in: *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, JohnWiley&Sons (1986), p. 227-23.