# The Contribution of Ultra-Fine Milling for the Microstruture and Density of the Doped Barium Hexaferrite Sintered Discs

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**Abstract:**

At first, the ferric oxide was ground in a roll mill, and then this product was submitted to planetary ball milling. Separately, the milled iron oxide samples (ultra-finely milled) were put mixed with stoichiometric amounts of barium carbonate and doping elements and then calcined (1) at 1350°C during 4 hours.

That sample coming from ultra-fine milling prior to calcination was again submitted to a final ultra-fine milling in a planetary ball mill. The doped barium hexaferrite final powder was granulated through spray drying and die-pressed into discs, which were subsequently sintered at 1350°C. These sintered pieces were characterized by scanning electron microscopy, X-ray diffraction (2) and magnetic characterization.

**Keywords:** barium hexaferrite, ultra-fine milling, microstructure, characterization and hysteresis.

## Introduction

During the past decade, the W-type hexaferrites having a general formula $XMe_2Fe_{16}O_{27}$ ($G^{2+}$ = Ba, Sr, La; Me = Zn, Co, Mn, etc) have attracted growing interest due to the large variety of properties they present.

Hexagonal ferrites are a family of hexagonal or rhomboedral ferrimagnetic oxides. Their crystal structure can be described by a superposition sequence of the fundamental structural blocks S, R and T representing two, three or four oxygen layers. For W structures, the divalent cations are located in octahedral, tetrahedral and five-fold coordination intersites. Their unit cell is the result of the superposition of two spinels blocks (S) and the hexagonal block (R) containing the heavy $Ba^{2+}$ or $Sr^{2+}$ ions.

The $Me^{2+}$ and $Fe^{3+}$ cations are distributed among seven different sublattices. There are 12 k octahedral sites, 4 e tetrahedral sites, 4 fIV tetrahedral sites, 4 fIV octahedral sites, 6 g octahedral sites, 4 f octahedral sites, 2 d hexahedral sites. The R and S units share the 12 iron sites in the k sublattice. The divalent cations $Mn^{2+}$ prefers to occupy lattice sites with tetrahedral coordination in the oxide compounds and its has the same magnetic moment as $Fe^{3+}$ and therefore will not perturb the net of the superexchange interactions among the various magnetic sublattice of the W-structure.

Barium ferrite compounds (compounds of barium, iron and oxygen) have been widely studied because of their magnetic properties. These compounds are well known as microwave and magneto-optical devices and show a promise in high-density magnetic recording media (3). The large applications (4, 5) are mainly due to the large coercivity and specific magnetic saturation of this low cost material. This low price is proceeding from the easy access to the oxide raw material, consisting of cheap and abundant elements and the relative easiness of manufacture.

The use of the ultrafine milling in the ceramic synthesis has been very studied in recent years. The ultrafine milling allows the ultrafine crystal production, with high specific area, high deformation, amorphous, with better chemical reactivity. These materials have important properties associated to the nanostructure so that the dense ceramic and composites obtained from these will show better sinterability.

The cominuition of fine and ultrafine particles is always a difficult and expensive operation. Some types of mills have been developed for the acceleration of the milling process. This equipment - called mills of high energy - is capable to produce intense fragmentation of materials through the energy application at high taxes. Examples of mills of high energy are the atritor, vibratory and the planetary. In the planetary mill the energy is transferred by the combination of the movements of rotation and translation of the jars that contain the load, causing the appearance of forces centrifugal machines and the acceleration of Coriolis. This equipment, available commercially, has been used successfully in the high milling of materials.

In the present work, it was carried out a study of the effects of the ultra-fine iron oxide milling, onto the density and microstructure of sintered discs of doped barium hexaferrite W-type, $BaMn_2Fe_{16}O_{27}$ to understand the magnetic properties of this material.

## Materials and Methods

W-type hexagonal ferrites were obtained using the conventional ceramic process. Diverse processes have been used in the synthesis of hexaferrites. The mixed oxide route detaches as one of the main paths with potential of industrial application, a time that allows the production in wide scale, when compared with other methods. The amount of doped W-type hexaferrite depends on the effectiveness of both the mechanical mixing of the batch and the diffusion occurring during calcination. The mixed oxide route is an effective and cheap method for the preparation of the materials, leading to the production of particles with small sizes and good uniformity.

Reagent grade barium carbonate and salts of the doping element, manganese oxide, were mixed to the finely ground iron oxide in order to make the doped barium hexaferrite. The starting iron oxide was supplied by Companhia Siderurgica Nacional (CSN, Brazil) and was produced at its steel-pickling line as by-product of the Spray-pyrolysis Acid Recovery Unit.

At first, such ferric oxide was ground in a roll mill, and then was submitted to planetary ball milling. Separately, the milled iron oxide samples (ultra-finely milled) were put mixed with stoichiometric amounts of barium carbonate and doping elements and then calcined at 1350°C during 4 hours.

A path, that consists of the planetary milling in double period of training (30 min in dry milling and 45 min in wet milling) - with grinding bodies of different types and densities - was used for the oxide milling of iron for use in the production of W-type barium hexaferrite.

It was demonstrated that it is possible to get a product with specification the desired (so great medium of 0.38 μm, high uniformity, with only 5% greater that 1 mm and high pureness) from granules of some millimeters in a modest time of milling (1 h and 15 min). (6)

Iron oxide samples ($Fe_2O_3$) proceeding from the URA of the CSN had been used. The purity of the material determined for spectrometry of fluorescence of rays-X was of 99.36% of $Fe_2O_3$ that is satisfactory so that the doped barium hexaferrite presents good magnetic properties. The main joined contaminants had been the manganese oxide (0.35% of $MnO_2$), the silica (0.129% of $SiO_2$) and alumina (0.07% of $Al_2O_3$). Its specific density is of 4.8 g/cm$^3$.

Assays of planetary milling had been carried through in a mill PM-4 (of the Retsch). Diameter 10cm of and 500ml of volume had been used receiving cylindrical with, which is located diametrical to a rotation arm (with ray of 15cm). The mill is set in motion by an engine of Receiving 750W. of stainless steel, coated internally with tungsten carbide of had been used in the tests. Assays had been carried through with constant wadding degree (30%), with fulfilling of emptiness of 150% and the speed of rotation was 250 or 200 rpm. In the calculation of the wadding degree and the fulfilling of emptiness a porosity of the 40% load was assumed. (6)

That sample coming from ultra-fine milling prior to calcinations was again submitted to a final wet ultra-fine milling in a planetary ball mill. The doped barium hexaferrite final powder was granulated through spray drying and die-pressed into discs, which were subsequently sintered at 1350°C.

These sintered pieces were characterized by scanning electron microscopy (Figures 3 to 6) and X-ray diffraction (Figure 7).

## Results and discussion

X-ray fluorescence, Energy Dispersive Spectroscopy (EDS), scanning electron microscopy and X-ray diffraction using Cu Kα radiation were then used to characterize the calcined powder. X-ray fluorescence and EDS confirm that the powder was obtained at the correct stoichiometry.

Figure 1 shows the representative Energy Dispersive Spectroscopy for different places of the sample. All the samples analyzed the EDS had the same shape. In this illustration we can observe the very pronounced picks of the elements Fe, Ba and Mn, as it was waited.

The picks of the element Au due to the fact of the samples were covered with gold. Al's pick is already due to the fact of the support to be constituted of this element.

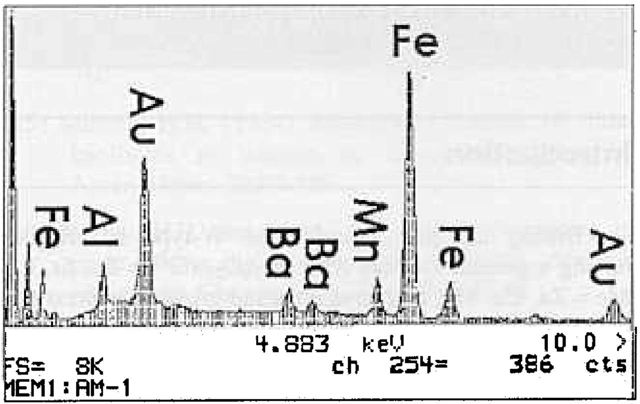

Figure 1 - Energy Dispersive Spectroscopy for different places of the sample.

The SEM of the calcined powder is showed in the Figure 2. We can see that the powder was really ultra-fined milled. The particles are very comminuted and the medium particle size is about 0.3 μm.

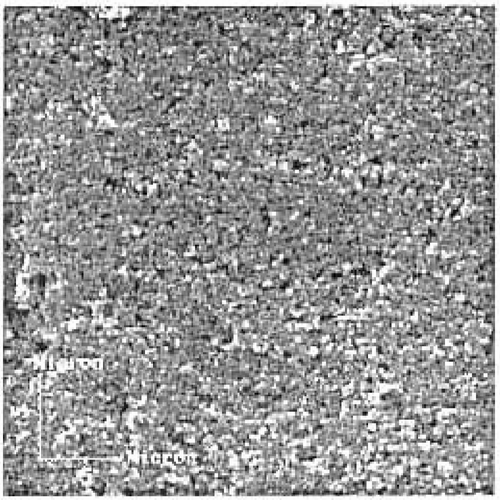

Figure 2 – SEM micrograph of calcined powder at 2000X

The sintered pieces were characterized by scanning electron microscopy (see Figures 3 to 6).

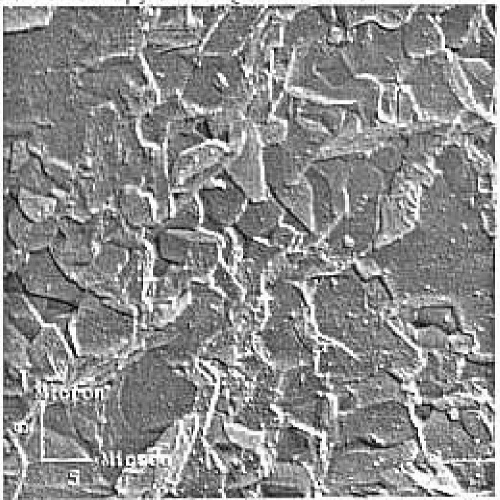

Figure 3 – SEM micrograph of the sample at 2000X. This figure reveals the high density of the sample

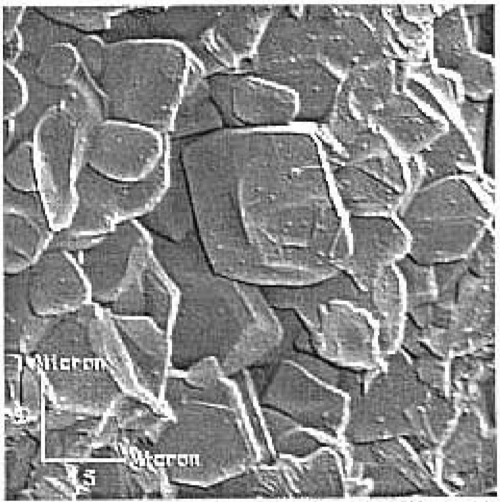

Figure 4 - SEM micrograph of the sample at 3000X. In this figure we can see the real shape and size of the grains (about 5µm)

Figure 5 - SEM micrograph of the sample submitted to chemical attack (HCl at 80°C during 30 s) at 2000X. In this figure, we can see the grain boundaries of the sample.

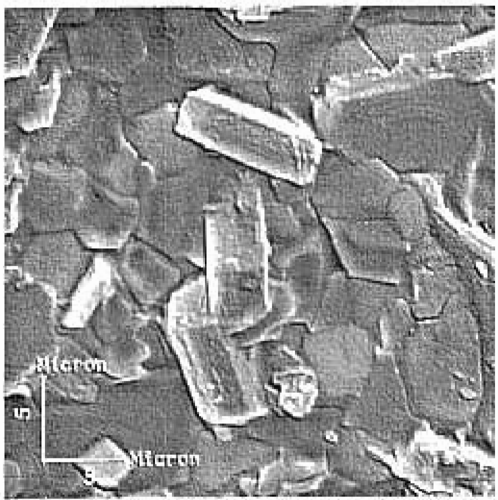

Figure 6 - SEM micrograph of the sample submitted to chemical attack (HCl at 80°C during 30 s) at 3000X. This figure shows that the sample has a high density and the grain size is about 5µm.

Figure 7 presents the X-ray pattern of the W-type hexaferrite after calcination at 1350°C for 4 h. This figure shows the formation of the desired phase.

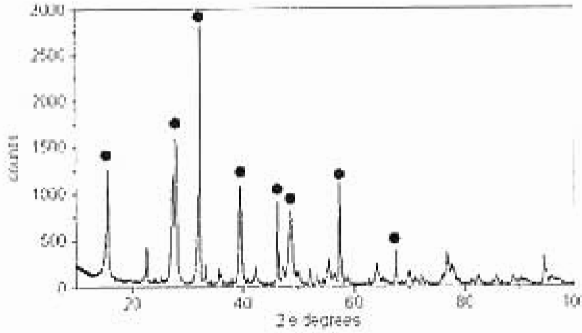

Figure 7 – X-ray pattern of the W-type hexaferrite (where: • $BaMn_2Fe_{16}O_{27}$).

The density of this material was determined by the Archimedes' Principle and it was 5.26 g/cm$^3$.

Figure 8(a) presents the hysteresis curve of the powder pieces calcined at 1350°C. The saturation magnetization $M_s$ was obtained by extrapolating M(1/H)-curves to 1/H = 0. The saturation magnetization value is 42.5 emu/g for this material.

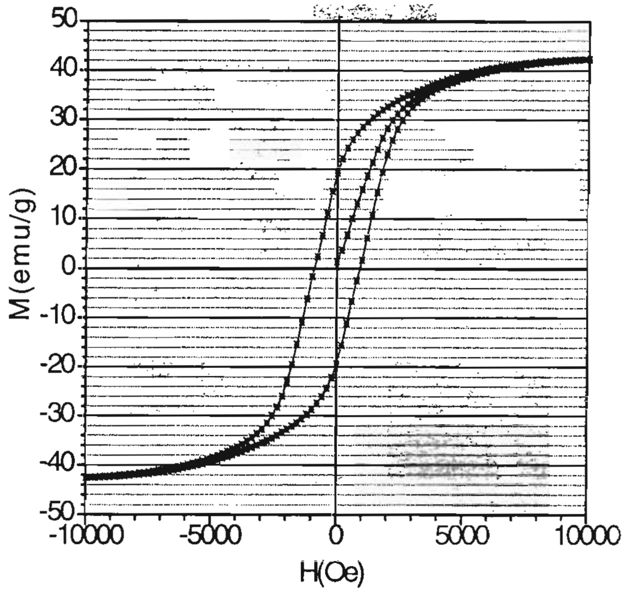

Figure 8(a) – Hysteresis curve of the powder calcined at 1350°C.

Figure 8(b) presents the $B_i$ (kG) versus H (kOe) graphs displaying the hysteresis loops of the ceramic pieces sintered at 1350°C. In this figure, $B_r = 657.3$ G, $H_c = 411$ Oe, $H_{max} = 10.01$ kOe and $B_{max} = 12.13$ kG.

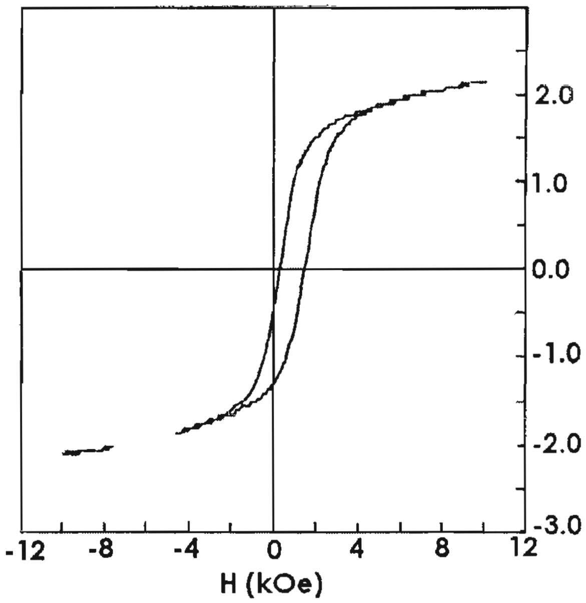

Figure 8(b) – Hysteresis curve of the sample sintered at 1350°C.

## Conclusions

The purity of the iron oxide from Companhia Siderurgica Nacional (CSN) looks satisfactory for the production of this doped barium hexaferrite and the contamination level during fine milling was low enough to meet the requirements for the final ceramics.

The use of ultra-finely ground feedstock seems to be promising for the sake of direct production of doped barium hexaferrite without the need of pre-calcination, as its results of microstructure and magnetic properties are comparable to those provided by the conventional powder mixing method.

For a given sintering time, the ultra-fine milling allows achieving full densification coupled to that, the corresponding grain-size was 5 µm.

The saturation magnetization value for the powder calcined at 1350°C was 42.5 emu/g.

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