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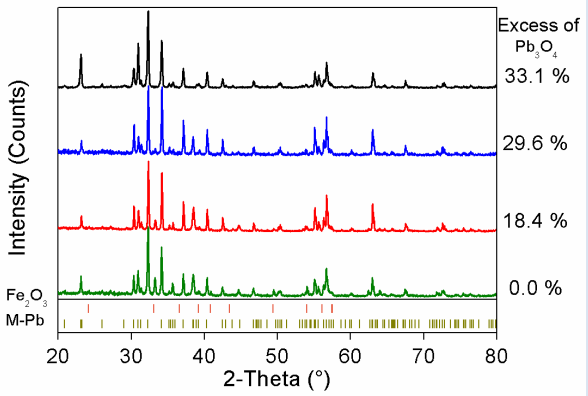
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STUDY OF THE MAGNETIC PROPERTIES OF THE PB-HEXAFERRITE OBTAINED AS A SINGLE PHASE BY TWO METHODS OF PREPARATION

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ABSTRACT

Pure lead hexaferrite ($PbFe_{12}O_{19}$) was obtained using two different methods of preparation, the solid state reaction and the chemical coprecipitation. It was found that the lead hexaferrite prepared by the solid state method is obtained without secondary phases by adding 33.09 % of lead oxide as an excess and sintering at 950 °C during one hour, also the pure lead hexaferrite prepared by the coprecipitation method is obtained at 700 °C without lead losses. We studied the structural and magnetic properties of both samples, a remarkable increase was found in the coercivity field of the sample prepared by coprecipitation as well as a reduction of the magnetic saturation, compared with the sample prepared by the solid state reaction. This behavior is attributed to the morphologic characteristics and the microstructure that is obtained in an inherently way to the preparation method.

Keywords: Magnetic Ceramics; X-Rays; Rietveld refinement; Chemical coprecipitation; Solid-state reaction.

ESTUDIO DE LAS PROPIEDADES MAGNÉTICAS DE PB-HEXAFERRITA OBTENIDA EN SU FASE PURA POR DOS MÉTODOS DE PREPARACIÓN

RESUMEN

La hexaferrita de plomo ($PbFe_{12}O_{19}$) ha sido obtenida de forma pura utilizando dos métodos de preparación diferentes, el método de reacción en estado sólido y el método de coprecipitación química. Se encontró que la hexaferrita de plomo preparada por el método de reacción en estado sólido se obtiene al añadir 33.09 % en exceso de óxido de plomo, sinterizando a 950 °C durante una hora. Por otro lado, la hexaferrita preparada por coprecipitación química se obtiene de forma pura a partir de 700 °C, sin añadir exceso alguno de plomo. Se estudiaron las propiedades magnéticas y estructurales de ambas muestras. Se encontró un marcado incremento en el campo coercitivo de la muestra preparada por coprecipitación así como una disminución en la magnetización de saturación comparada con la obtenida por el método de reacción en estado sólido. Este comportamiento se atribuye a las características morfológicas y micro-estructurales inherentes a cada método de preparación.

Palabras Claves: Cerámicas magnéticas; Rayos X; Refinamiento Rietveld; Coprecipitación química; Reacción en estado sólido.

1. INTRODUCTION

Hexagonal ferrites with general formula $MFe_{12}O_{19}$ (M = La, Ba, Sr, Pb), are hard ferrites with ferrimagnetic order used as permanent magnets [1]. They have technological interest because possess magnetic properties, strong magneto-crystalline anisotropy, high chemical stability [1-2], besides its low cost of fabrication. The specific interest on the lead hexaferrite lies on the low temperature at which the magnetic phase is formed [3], compared with the barium [4] or the strontium hexaferrite [5], both formed at temperatures above 1250 °C, or the lanthanum hexaferrite formed at 1360 °C [6].

The success in obtaining the pure lead hexaferrite prepared by the ceramic method lies in determining the amount of lead that is lost during the heat treatment; this loss of lead was determined using the Rietveld method to make a quantitative analysis of phases. Although the lead hexaferrite has been obtained before [7-10], in most of the reports, the hematite is also present due the loss of lead [11]; in these cases, the properties and the interpretation corresponds to a mixture of interacting phases and not to the pure lead hexaferrite. Traditionally, empirical or approximated methods were used to compensate these loss of lead [12, 13], or complicated methods are used to obtain the phase by adding lead in an empirical fashion [3, 14].

In this work, we report the optimal conditions at which the pure lead hexaferrite is obtained using two different methods of preparation: the solid state reaction method and the chemical coprecipitation method; also the magnetic and structural behavior of the lead hexaferrite was analyzed when prepared by these methods.

2. EXPERIMENTAL PART

In order to determine the optimal conditions to obtain pure lead hexaferrite we prepared it using the solid state reaction method and the chemical coprecipitation method. The ceramic method involves the solid-state reaction of oxides or carbonates powders at high sintering temperature. By other way, the coprecipitation method consists of the simultaneous precipitation of iron and lead hydroxides by a NaOH solution and sintering the powders at lower temperatures. In both cases, the conditions of crystallizing were investigated varying the sintering temperature and time. The conditions reported here, result the best conditions to obtain the pure lead hexaferrite using the solid state reaction and the chemical coprecipitation methods.

2.1 Ceramic method

The solid state reaction method was used via three basic steps: powder milling, green body forming and sample sintering. The precursors of the lead hexaferrite were hematite, α-Fe_2O_3, and lead oxide, Pb_3O_4. The solid-state reaction is described by $2Pb_3O_4 + 36Fe_2O_3 \rightarrow 6PbFe_{12}O_{19} + O_2$. The powders were mixed with ethanol and subjected to ball-milling for 2 hours at 90 rpm; thereafter, the powders were heat-treated in air at 950 °C during 120 minutes. The result of the quantitative analysis of phases made by the Rietveld analysis showed that 14.60 %, in weight, corresponds to hematite secondary phase and the rest is lead hexaferrite. A calculated lead oxide excess was added to the powders to react with the remaining hematite. The powders were newly mixed and sintered at 950 °C during two hours, a new analysis of phases was made and the results showed a decrease of the remaining hematite, staying in 8.9 % wt. Again, it was calculated the lead oxide that react with the remaining hematite and it was added as an excess, then powders were sintered at 950°C. The above procedure was repeated twice and finally the pure lead hexaferrite was obtained by adding 33.09 % wt. of lead oxide. Considering the previous result, it was prepared a sample of pure lead hexaferrite in one step by adding 33.09 % in excess of lead oxide and sintered at 950 °C during two hours, this sample was tagged as PBM1.

2.2 Chemical coprecipitation method

The chemical coprecipitation method is based on the simultaneous precipitation of particles (iron and lead hydroxides) that serve as chemical precursors of the lead hexaferrite. $Fe(NO_3)_3 \cdot 9H_2O$ and $Pb(NO_3)_3$ both were mixed in stoichiometric ratio and dissolved in deionized water. The admixture was slowly dropped in a NaOH solution with pH = 12.0 and it was continuously agitated maintaining the temperature at 60 °C. The resulting precipitated powders were washed and filtered with deionized water until pH = 7.0 was obtained. Finally the powders were heat-treated in air at 700 °C during 60 min, this sample was tagged as PBM2.

2.3 Characterization

The structural characterization of both samples was

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made by means of X-ray diffraction at room temperature with a GBC Enhanced Mini-Materials Analyzer, Cu (Kα) radiation in the Bragg–Brentano geometry. The Rietveld method, incorporated in the MAUD program, was used to refine the crystal structure and for quantitative phase analysis [15]. The magnetic characterization was made by the obtainment of their hysteresis loops at room temperature with a LDJ Electronics VSM9600 vibrating sample magnetometer with a maximum applied field of 12 KOe. The morphologic characteristics of the samples were studied using a Jeol 1200 electron microscope working at 120 kV.

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffractograms of the a) PBM1; b) PBM2 samples and indicating the diffraction angles in 2-Theta of the hematite (Fe_2O_3) and of the lead hexaferrite (M-Pb) phases. In both cases it is possible to see that hematite is not present in these samples, only the M-type hexaferrite. This indicates that lead hexaferrite was obtained as single phase through these two methods of preparation under the conditions described above for each one. Figure 2 shows a thermogravimetric analysis of the powders prepared by coprecipitation, here is indicated that the Pb-hexaferrite phase crystallizes around of 700 °C, without loss of lead. This result is in agreement with the X-rays analysis. The structural characterization was obtained through the refinement of the crystal parameters by the Rietveld method. The results of the refinement of the structure of the analyzed samples are present in Table 1.

From the results of the crystal structure refinement we can see a variation in the density of the samples that is related with a change of the parameters *a,* and *c* of the unit cell. The cell parameters tend to be smaller and consequently, the density is bigger in the sample prepared via the solid state reaction method. This behavior is only attributed to the different sintering temperatures used. In PBM1 sample the sintering temperature was 950 °C, in contrast with the PBM2 sample, (700°C) which has not been reported before. The samples prepared by the coprecipitation technique did not present loss of lead due the temperature used to sintering the powder is lower than the temperature at which the lead evaporates (~900 °C) [16]. Another remarkable result is the diminishing in the crystallite size of the PBM2 sample prepared by the coprecipitation method, in this case the obtained crystallite size is only of 53 nm compared with the crystallite size obtained in the PBM1 sample with size of 161 nm. The reduction in the crystallite size is attributed to the small size of the precipitated particles that is possible to obtain by coprecipitation, also the reduced sintering temperature prevents the growth of crystallites [17].

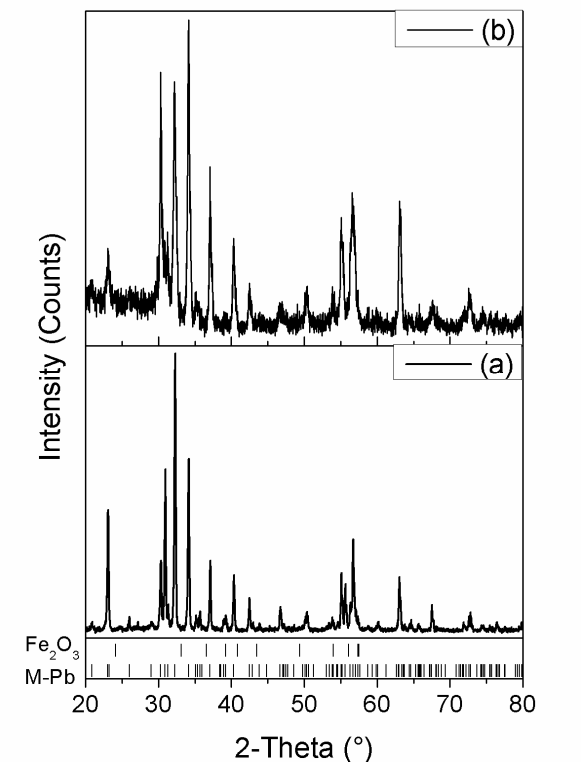


Figure 1. X-ray diffractogram of the sample prepared by a) the ceramic method (PBM1) and b) the coprecipitation method (PBM2).

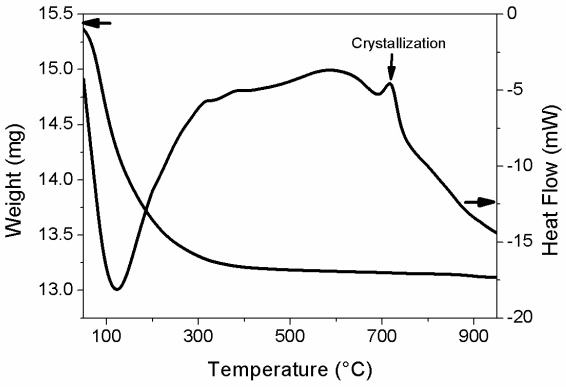


Figure 2. TGA-DTA analysis of the precursor powder of the lead hexaferrite prepared by coprecipitation.

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Table 1. Rietveld refinement results of the samples PBM1 and PBM2.

Sample	*Sintering temperature (°C)*	*Cell parameter (Å)*	*Crystallite size (nm)*	*Density (g/cm^3)*
PBM1	950	a = 5.8939 (2) c = 23.1290 (5)	161 (1)	5.77
PBM2	700	a = 5.8955 (4) c = 23.2299 (9)	53 (1)	5.61

The magnetic characterization was made with vibrating sample magnetometry (VSM). It were obtained the hysteresis loops of both PBM1 and PBM2 samples by applying a maximum magnetic field of 12 KOe, in order to saturate the samples; the parameters analyzed through this method were the magnetic saturation (σ_s), the magnetic remanence (σ_r), and the coercivity field (H_c), additionally, from the initial curve of magnetization we obtain the initial susceptibility (χ_{in}). The behavior of the initial curve of the hysteresis loop gives information about the presence of structural defects or disorder that plays a dominant role in the magnetizations process. The initial susceptibility χ_{in} is described by the equation (1).

$$\chi_{in} = H_{app}/M \qquad (1)$$

where H_{app} is the applied magnetic field and M is the magnetization. The initial susceptibility is obtained in the linear region at low values of applied field.

The hysteresis loops of the PBM1 and PBM2 samples are shown in Figure 3. The PBM1 sample has higher value of remanence and saturation, however, the PBM2 sample has higher value of the coercive field. In Table 2 the results of the magnetic characterization of both samples are indicated. The magnetic saturation is determined using the law of approximation to the saturation [18], as consequence of the high magnetocrystalline anisotropy of powders randomly oriented. Thus, the crystallites oriented perpendicularly to the magnetic field reaches the saturation at a very high magnetic field.

Table 2. Results of the magnetic characterization.

Sample	σ_s *(emu/g)*	σ_r *(emu/g)*	H_c *(KOe)*	χ_{in}
PBM1	72.0	39.0	1.7	0.0129
PBM2	38.3	20.0	3.5	0.0031

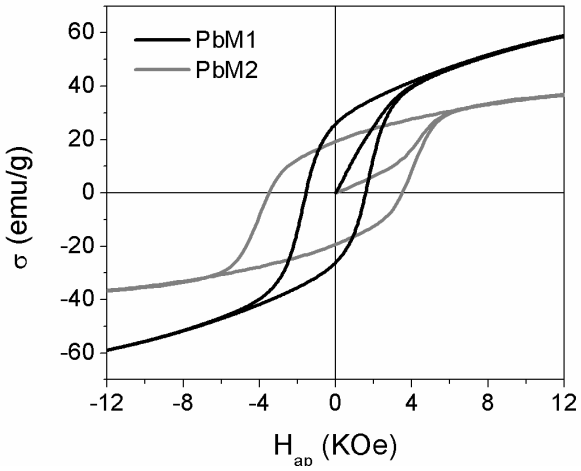


Figure 3. Hysteresis loops of the PBM1 and PBM2 samples.

Differences in the magnetic behavior observed from the hysteresis loops of the PBM1 and PBM2 samples are attributed to the interparticle interaction and to the way in which this interactions take place, in most of the cases is very complicated and related to the form, size and distribution of the particles which in turn depend on the way of the hexaferrite is prepared.

The initial susceptibility of the PBM2 sample indicates that the magnetization reversal is mainly controlled by the pinning of the wall motion produced by structural defects which act as anchoring centers, when the applied field increases above a critical (H_p), the defects which oppose to the wall motion are exceeded and the initial curve reaches the saturation in an easy way. For the PBM2 sample the H_p is about 4.0 KOe. In contrast, in the PBM1 sample the pinning are negligible and the reversal magnetization is controlled mainly by nucleation of inverse domains. Then for the same

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compound we can see two different behaviors in reversal magnetization, these behavior and the differences in magnetic properties can be explained in terms of the microstructure acquired from the use of each method of preparation.

The differences in the magnetic parameters can be explained in terms of the microstructural characteristics of the samples. The morphology and grain size were studied using scanning electronic microscopy (SEM). For the PBM1 sample, it was found that the morphology of the particles was hexagonal platelets with an average particle size of 2.0 µm, see Figure 4A. In the case of the PBM2 sample, the particles are shown as agglomerates of small wires which tend to form big particles by effect of the diffusion of the atoms with the increase of the sintering temperature. In Figure 4B the micrograph of the PBM2 sample is presented.

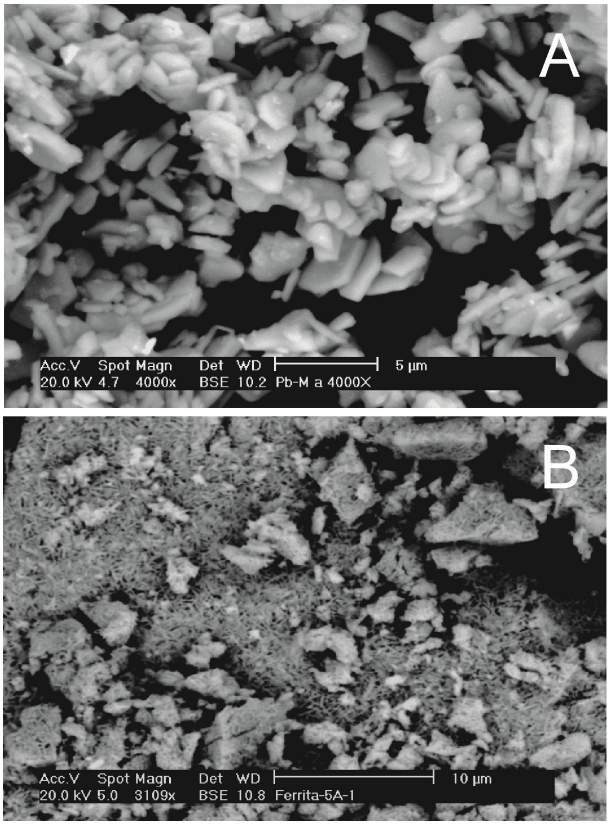


Figure 4. SEM micrographs of the PBM1 sample (A) and the PBM2 sample (B).

The lower magnetization of the PBM2 sample is attributed to the porosity of the agglomerates; in this case the demagnetizing field produced in the pores could be large, then the magnetization of the system tend to diminish. Some investigations are carried out to understand the effect of the pores in different magnetic systems [19, 20]; is well known that small grain sizes are related with high values of coercivity [20, 21]. Then, the small grain sizes of the particles obtained in the PBM2 generated an increase in the coercivity field, and when the particles size increases the coercivity decreased, as in the PBM1 sample.

4. CONCLUSIONS

The lead hexaferrite was successful obtained without secondary phases using two methods of preparation: the solid state reaction method and the chemical coprecipitation method. For the obtainment of the hexaferrite using the ceramic method, it was developed a successfully simple technique which allows to obtain the pure phase in one single step, consisting of adding an excess of 33.09 % of lead oxide to the stoichiometric formula and by sintering at 950 °C during one hour. In the case of the lead hexaferrite obtained at 700 °C by coprecipitation, the high porosity reduces its magnetization, and the small size of particles helps to reach the high value of coercive field. The differences observed in the morphology and grain size act directly on the magnetic properties of the hexaferrite through the variation of the coercivity field, the magnetic saturation and the magnetic susceptibility as function of the microstructure.

The reversal magnetization of the lead hexaferrite also depends on the method of preparation, due to introduction of pining centers that hinder the magnetization process, increasing the coercivity field. Typically, lead hexaferrite has low coercivity as showing the results obtained from the sample prepared by the solid state reaction method.

5. ACKNOWLEDGMENTS

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