First order reversal curves analysis of the temperature effect on magnetic interactions in barium ferrite with La-Co addition

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Abstract

First order reversal curves (FORC) distributions are a powerful tool for investigating hysteresis and interactions in magnetic systems and have been widely applied. La-Co substitution in barium hexaferrites has also been extensively studied. The most effective substitution to improve the magnetic properties (coercive field and energy product) is given by $x = y = 0.2$ in the formula Ba_{1-x} La_x Fe_{12-y} Co_y O_{19}. In this work, this stoichiometry is initially used to obtain a state where more than one phase is present. The magnetic behavior as a function of temperature was studied in order to have an insight into the magnetic interactions that originate a decrease in the magnetic performance of Ba hexaferrite magnets. The sample was structurally characterized by x-ray diffraction (XRD) and magnetically studied in a SQUID magnetometer. FORC distributions were used to study the dependence of the magnetic interactions with the temperature. FORC diagrams performed on the sample at different temperatures exhibit similar characteristics, such as the spread in the h_c – h_u plane and a spread out of the h_c axes. These features are interpreted in terms of exchange-interacting particles and dipolar interactions, respectively. As the temperature decreases, stronger interactions are noticed among hard and soft phases.

Key words: Barium hexaferrite, FORC distribution, La-Co substitution.
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Magnetic ferrites are a commercial magnet material widely employed in technological applications because of their low-cost production as well as their good performance. In order to improve their magnetic performance, structural and magnetic properties have been studied and modeled. In general, these studies are devoted to understanding and/or explaining the coercive field, anisotropy field or the role of the interactions in the magnetization process [1–7]. Also doping and substitution with Ti [8], Al [9], La, Co among other elements have been tested [3,10]. The usually observed temperature dependence of the magnetic parameters plays an important role in the final products because these materials are used in many applications which cover a wide temperature range. When the temperature varies the magnetic interactions between the grains of sample also vary and different magnetic behaviors are noticeable.

When the stoichiometry is not precise or the fabrication process is not adequate the ferritic phase is accompanied by other phases that promote magnetic interactions which result in a decrease of the magnetic performance of the magnets.

In recent years, First Order Reversal Curves (FORCs) became an efficient tool to investigate and describe the magnetic hysteretic behavior of systems of particles and their interactions by means of a FORC diagram [3,5,10–12]. In order to calculate a FORC diagram, a family of FORCs with different reversal fields is measured, being $M(H_\alpha, H_\beta)$ the resulting magnetization as a function of both the reversal H_α and applied H_β fields, as depicted in Fig. 1.

Using the equation shown at the bottom of Fig.1

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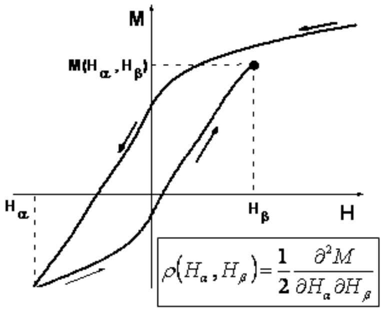

Fig. 1. Scheme of a FORC measurement and involved variables.

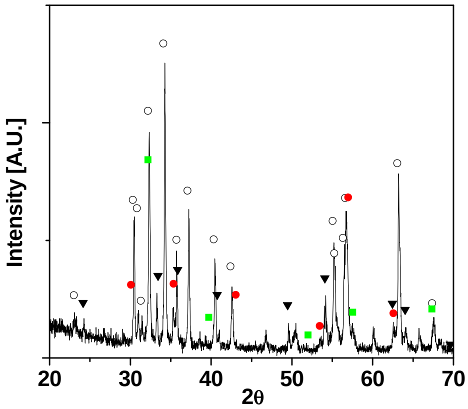

Fig. 2. X-ray diffraction pattern. Open circles: $BaFe_{12}O_{19}$, solid (red) circles:$CoFe_2O_4$, solid (black) traingles: Fe_2O_3, solid (green) squares: $LaFeO_3$

and changing variables to the local coercivity $h_c = (H_\beta - H_\alpha)/2$ and the local bias $h_u = (H_\beta + H_\alpha)/2$, the FORC distribution $\rho(h_c, h_u)$ can be obtained. A FORC diagram is a contour plot of a FORC distribution. A more detailed explanation of the FORC model and its experimental implementation has been done in previous works [3,5,10].

In the present work the aim was focused on the study of magnetic interactions among the phases which are present in doped barium hexaferrite, when secondary phases appear.

The conventional ball-milling process was employed to obtain the studied system. The precursor oxides to form $Ba_{0.8}$ $La_{0.2}$ $Fe_{11.8}$ $Co_{0.2}$ O_{19}—barium carbonate ($BaCO_3$), hematite (Fe_2O_3), lanthanum oxide (La_2O_3) and cobalt acetate— were mixed in stoichiometric proportions and milled for 100 hours at 200 rpm in air atmosphere in a planetary ball-mill with a ball/powder ratio of 3.

The as-milled powder was heat-treated in air atmosphere for 6 h at 1000°C. The characterization by x-

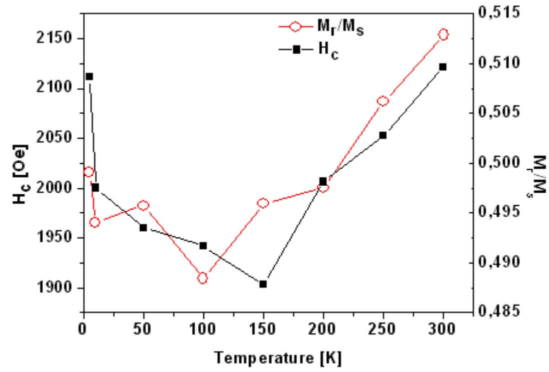

Fig. 3. Coercive field and M_r/M_S as function of temperature.

ray diffraction (XRD) with CuK_α radiation shows that barium hexaferrite has not completely crystallized after the thermal treatment. Small amounts of hematite still remain without transforming and segregation of secondary phases such as $CoFe_2O_4$ and $LaFeO_3$ is observed (Fig.2). According to XRD data, the different phases appear in the following proportions: 59% hexaferrite, 14% cobaltite, 18% hematite and 9% La orthoferrite. From magnetic measurements at 5K, saturation magnetization M_S of the sample was determined to be 70 emu/g. Considering the reported values of M_S at 0K for Ba hexaferrite (100 emu/g [13]) and cobaltite (90 emu/g [13]) and their proportional contribution to the sample magnetization, a calculated $M_S^{\rm calc} = 71.6$ emu/g was obtained. This value —obtained without considering neither hematite nor La orthoferrite contributions— is in good agreement with the measured M_S and supports the idea of disregarding weakly ferromagnetic Fe_2O_3 and antiferromagnetic $LaFeO_3$ in the analysis of magnetic interactions.

This sample was therefore chosen to study the magnetic interaction between particles of hexaferrite (hard phase) and cobaltite $CoFe_2O_4$ (softer phase, designated as 'soft' from now on).

The magnetic properties of the sample were studied in a SQUID magnetometer with a maximum applied field of 20 kOe. The coercive field H_c and the ratio of remanent to saturation magnetization M_r/M_S were obtained from the major hysteresis loops and are shown in Fig.3. Both coercivity and M_r/M_S have a similar evolution with the temperature variation. When the sample is cooled down from room temperature both H_c and M_r/M_S decrease, reaching their lower values at 150K and 100K, respectively. When lowering the temperature below 100K these variables increase.

It is generally accepted that a decrease in coercivity is associated to an increase in exchange interactions (see, for instance, ref. [15]). Having this in mind, the behavior of H_c *vs.* T shown in Fig. 3 would indicate an increase in exchange interactions from 300K to 150K

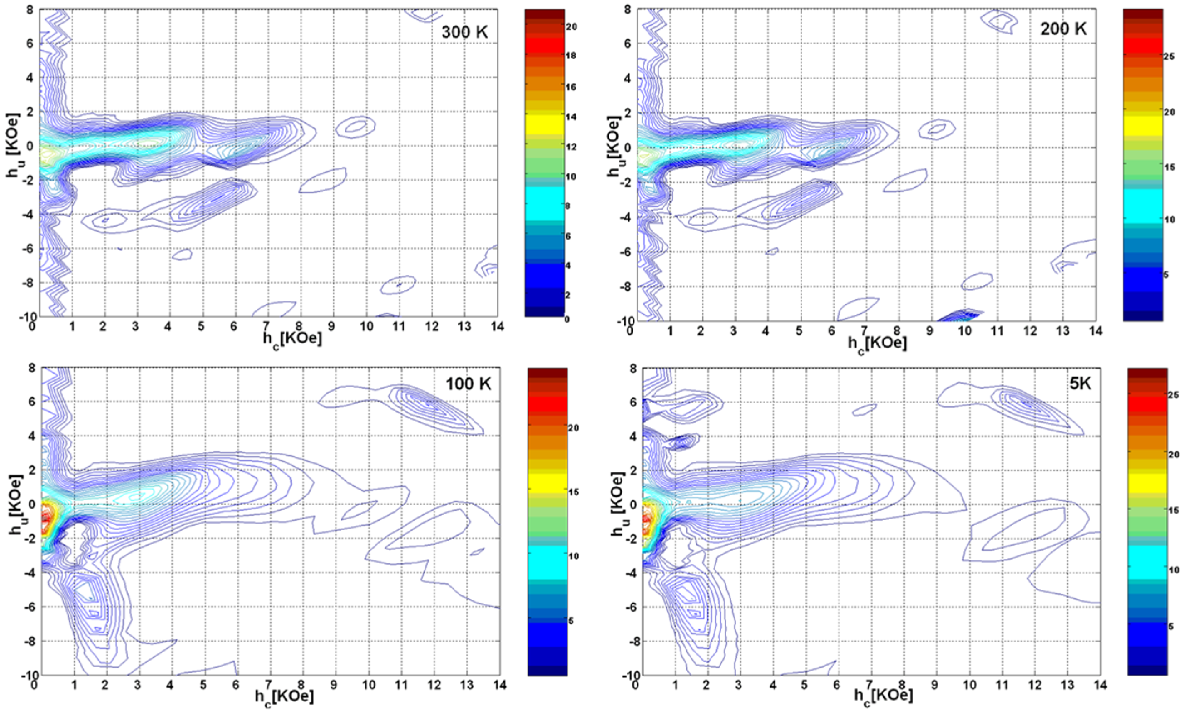

Fig. 4. FORC diagrams for 300K , 200K, 100K and 5K.

and a decrease from 150K to 5K.

In the whole temperature range the sample exhibits small differences with the value 0.5 for the ratio M_r/M_S predicted by Stoner and Wohlfarth [14] for a system of non-interacting particles. Above 225K the interactions are magnetizing and below this temperature a demagnetizing character is observed.

The FORC diagrams shown in Fig.4 have peaks extended in the $h_c - h_u$ plane. The observed peaks in the $h_c - h_u$ plane are typical of samples with hard and soft magnetic interacting clusters with dipolar and exchange interactions [11,17]. For 300K and 200K there is a low-h_c peak centered in 0.25 kOe and 0.2 kOe, respectively, and a high-h_c peak at 3 kOe. The spread of the distribution along the h_c axis indicates strong exchange-interaction between soft and hard particles and between hard particles and also to the presence of clusters of different size (see below). This interaction is the responsible for the magnetic hardening of particles or clusters with low coercivity (soft phase) and for the softening of particles or clusters with higher coercivity (hard phase).

The switching field H_{sw} of each cluster of particles can be associated with the coordinate h_c of each maximum in the FORC distribution [3,5,16]. In the sample there is a distribution of clusters with different number of particles and each type of cluster produces a peak in the FORC distribution. As a result of exchange-interactions, the switching field of each cluster is not equal to the switching field of an isolated particle because the anisotropy constant is reduced in the regions near internal surfaces, where the exchange-coupling occurs. Then, the exchange-coupling only takes place in a layer of depth l_w in each particle and this coupling induces changes in the orientation of spins, lowering the anisotropy energy within l_w. A particle that is exchange-coupled with only one neighbor has a higher switching field than a particle with two exchange-coupled neighbors, this one has in time a higher H_{sw} than the one with three, and so on. With this in mind, we can define an effective anisotropy constant $K_{eff} = K_1\alpha_{ex}$ that depends on the number of exchange-coupled neighbors and which is a mean value of the anisotropy constant in coupled and uncoupled regions. K_{eff} also depends on the extent of the interactions. All these factors are ascribed to the factor α_{ex}. When $\alpha_{ex} = 1$ the whole particle is uncoupled and if $\alpha_{ex} < 1$, there are some regions where exchange interactions are relevant.

In the case studied in this paper, two main exchange interactions are present —among hard-phase particles and among hard- and soft-phase particles. The FORC diagrams shown in Fig. 4 for $T = 300$K and $T = 200$K indicate that hard-hard interactions are present and are the responsible for the observed peak at 3 kOe. Because the low-field peak is continuously connected to the high-field peak, it is inferred that clusters of hard-phase particles must also contain some soft-phase particles, which are the responsible for a further lowering of K_{eff} in the hard phase. At the same time, the presence of hard-soft interactions favors a hardening of the soft phase.

The peaks along the h_u axis are due to soft particles that are under the influence of a dipolar field due to hard particles. The dipolar field H_d is oriented in the opposite direction of magnetization as a consequence of the hard particles that surround a given soft particle. At the beginning of a FORC cycle both magnetization and the applied field point towards the up (+) direction. When the applied field H goes from H_α to $H = 0$ the dipolar field created by the hard particles points to the down (-) direction, and when $H = -H_d$ the effective field acting on the soft particle will be $H_{eff} = 0$ and the magnetization of the soft particle will switch from the (+) to the (−) direction.

When the applied field goes from $H = 0$ to $H = -H_\alpha$, the dipolar field is in the same direction as the applied field. When hard particles start to invert their magnetization, the dipolar field is again opposite to the applied field and the magnetization of the soft phase switches back to the (+) direction.

This is what originates the distribution of peaks along the h_u axis, with $h_c = 0$.

The FORC diagrams at 100K and 5K show that the low-temperature peak has a much larger amplitude than it had for higher T and it is visibly hardened by the hard phase. It is also observed that peaks with $h_u < 0$ represent a hardening of soft particles since the distribution along $h_c = 0$ observed at high T is now shifted towards $h_c > 0$. At the same time, the main distribution along the h_c axis ($h_u = 0$) shows a shifting towards higher fields when comparing to the observed ones at higher T. This is probably due to a decrease of l_w at low T as a result of a higher anisotropy energy K_1, producing less hard-hard exchange interactions at low T. Also, this effect would probably make more effective the hard-soft interactions.

In these diagrams the high-field peak maintains its position but its amplitude is very much lowered when compared to the same peak at 300K and 200K, but at the same time it is extended toward higher h_c values. This is an evidence that non-interacting particles appear, indicating a lower l_w at low T. This fact can be summarized in a temperature-dependent α_{ex} parameter, being lower at higher temperature. This could be due to a decrease in the exchange length l_w for decreasing T. This is consistent with the variation of H_c with T, as shown in Fig.3. This behavior however, needs further study.

In summary, the low coercivity peak in the FORC diagrams is attributed to cobaltite and the high coercivity peak to the hexaferrite. When lowering the temperature the interactions between the soft and hard phases dominate the soft-soft and hard-hard interactions thus resulting in a magnitude diminution of the 3 kOe peak in favor of the low-field peak; that is to say, cobaltite softens the hard phase. Notwithstanding, the macroscopic value of coercivity at 5K is the same than the obtained at 300K (see Fig. 3). The displacement of the low-field peak to negative values of h_u at low temperatures proves that the soft particles are also influenced by the harder ones.

In conclusion, temperature changes affect the exchange-coupling interaction modifying the exchange-coupled volume in each particle and thus the magnetic properties of the sample. FORC diagrams are a useful tool to reveal how the interaction is affected by temperature, showing details that could not have been noticed by conventional magnetic properties measurements.

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