

MECHANOCHEMICALLY ASSISTED SYNTHESIS OF YTTRIUM-LANTHANUM ORTHOERRITE: STRUCTURAL AND MAGNETIC CHARACTERIZATION

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Abstract

Polycrystalline $Y_{0.5}La_{0.5}FeO_3$ powder was synthesized by mechanochemical activation of Fe_3O_4 - La_2O_3 - Y_2O_3 reactive mixtures. X-ray diffraction was used to follow the evolution of the formation of this orthoferrite. Peaks corresponding to reactants were no longer observed after 3h of activation, showing the completion of the reaction after this time. Magnetic hysteresis loops measured at room temperature revealed a gradual decrease of saturation magnetization, consistent with the consumption of ferrimagnetic Fe_3O_4 and the formation of antiferromagnetic $Y_{0.5}La_{0.5}FeO_3$. However, a small ferromagnetic contribution was observed even after 3 h of milling, which can be attributed to a canting in the alignment of the two sub-lattices in the orthoferrite structure. This uncompensated antiferromagnetism disappeared when the solid was heated, giving rise to a nearly antiferromagnetic structure.

Keywords: A. magnetically ordered materials, B. mechanochemical processing, D. magnetic measurements

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INTRODUCTION

Perovskites are mixed oxides with general formula ABO_3 . One of the distinctive characteristics of this family of inorganic compounds is the enormous variety of ionic substitutions that its crystallographic structure accepts. The tetrahedral so-called *A* sites can be occupied by more than 25 elements, while about 50 different elements are able to occupy the octahedral *B* sites. All these possible structural modifications give rise to many of the interesting electric and magnetic properties of perovskites. In particular, when *B* sites are occupied by Fe^{3+} cations these oxides are called orthoferrites. Rare-earth orthoferrites have been studied in the last decades for applications in functional materials such as catalysts [3], magnetic materials [4], sensors [5] and electrode materials for fuel cells [6].

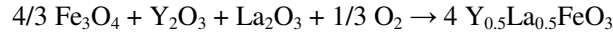
Lanthanum orthoferrite ($LaFeO_3$) has an antiferromagnetic structure which can be distorted by the substitution of La^{3+} by other trivalent cations, such as Gd^{3+} , Sm^{3+} or Yb^{3+} . These rare-earth elements significantly contribute to the overall magnetic response of the orthoferrites. In contrast, doping with non-magnetic Y^{3+} facilitates the analysis of the effect of the *A*-cation size on the magnetic properties of the compound.

It is a well-known fact that the properties of these materials are critically dependent on the synthesis method. Besides the conventional solid-state reaction method, several techniques based on innovative wet-chemistry have been introduced [7-9]. Although these preparative routes yield pure and homogeneous nano and microparticles, their processes of formation are frequently complicated and require the use of expensive and moisture-sensitive reagents. In this context, mechanochemical activation of solid reactants offers an interesting alternative method to synthesize orthoferrites. This relatively simple technique allows producing solid-state reactions at room temperature leading to high-purity phases. In the last decades this methodology has been applied to the preparation of metal alloys, composite materials and ceramic oxides [10-12]. High-energy impact and friction processes result in distortions and crystalline defects in the activated solids, favoring chemical reactions and eventually producing metastable phases. For this reason, the method results attractive for the formation of orthoferrites. Recently, the method was successfully employed in the synthesis of $LaFeO_3$ [13-14]. Different variables of the crystal structure, such as cation distribution, lattice geometry and magnetic ordering can be modified and controlled in this way [15-17]. As a consequence, novel physical phenomena and functional properties can be found.

The aim of this work is to determine the effect of both chemical doping and mechanochemical activation on the magnetic behavior of yttrium-lanthanum orthoferrite.

EXPERIMENTAL

A powder mixture of Fe_3O_4 (a magnetite concentrate ore, 97.5 %), La_2O_3 and Y_2O_3 (commercial reagents, 99.9%) was prepared according to the stoichiometry of the reaction



This mixture was mechanochemically activated in a Fritsch Pulverisette 7 planetary ball-mill, using balls and vials made of Cr-hardened steel. A ball-to-powder mass ratio of 20 and a rotation speed of 1500 rpm were used. The vials were opened several times during the milling process in order to ensure an appropriate oxygen supply. Small portions of powder were periodically withdrawn from the vial in order to analyze the evolution of the activation process. The series of samples was labelled YMLx, being x the activation time in hours.

The sample activated for 3h (YML3) was thermally treated at 600, 800 and 1000°C for 30 minutes under air atmosphere.

The composition of crystalline phases in all the samples was analyzed by X-ray diffraction (XRD) using a PW 1830/40 diffractometer at 40 kV and 30 mA, with $\text{CoK}\alpha$ radiation ($\lambda = 0.17890$ nm) and Fe filter. The following equation [18] was used for determining the lattice parameters of the orthoferrite phase:

$$1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2, \quad (1)$$

where d is the distance between crystalline planes with Miller indices $(h\ k\ l)$, and a , b , and c are the lattice parameters. From this expression, it is evident that the position of three XRD peaks must be determined in order to assess the parameters of an orthorhombic structure. Peaks belonging only to one signal and with a significant diffracted intensity were selected, corresponding to crystalline planes indexed as $(1\ 0\ 1)$, $(1\ 2\ 1)$ and $(2\ 2\ 0)$.

For each sample, magnetization (M) as a function of magnetic field (H) was registered at room temperature in a LakeShore 7300 vibrating sample magnetometer (VSM) coupled to an electromagnet able to produce a magnetic field up to 15 kOe.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the series of activated samples. At milling times shorter than 1 h (not shown) a significant decrease of intensity and broadening of the reactants peaks (Fe_3O_4 , La_2O_3 and Y_2O_3) is observed. This is due to the amorphization of the crystal structures and the decrease in grain sizes, respectively. From 1 h on, the appearance of peaks corresponding to the orthoferrite phase $\text{Y}_{0.5}\text{La}_{0.5}\text{FeO}_3$, together with the gradual disappearance

of reactants peaks can be noticed. Longer milling times do not lead to increased intensities, but only to broader peaks indicating a decrease in crystallite size of the synthesized phase. Calculations with Scherrer equation [18] indicate that the crystals of orthoferrite obtained after 3 h of activation are 13 nm in diameter.

Figure 2 shows the magnetic hysteresis loops measured for each activated sample. A continuous decrease of saturation magnetization (M_s) with milling time is clearly observed. This is a consequence of the loss of crystallinity of magnetite during the first 30 min of activation, and the formation of the antiferromagnetic $Y_{0.5}La_{0.5}FeO_3$ phase from 1 h on. The drop in M_s is particularly significant between 1 and 2 h of mechanical treatment, which confirms that the formation of the orthoferrite structure mainly occurs in this period. The progressive decrease in coercivity (H_c) is also consistent with the gradual formation of antiferromagnetic $Y_{0.5}La_{0.5}FeO_3$ at the expense of ferrimagnetic magnetite. The inset in Figure 2 shows the variation of M_s and H_c with activation time. Despite sample YML3 only contains $Y_{0.5}La_{0.5}FeO_3$, the magnetic response indicates a non-negligible residual magnetic moment, which is not expected for the orthoferrite antiferromagnetic structure. However, it is a well-known effect that in these perovskite structures the antiparallel spin ordering can be altered by the incorporation of A cations of different sizes leading to the tilting of FeO_6 octahedra and spin canting [19]. On the other hand, the mechanosynthesized $Y_{0.5}La_{0.5}FeO_3$ phase presents a distorted structure with an elevated number of defects which contributes to the disordered spin arrangement. This effect has been recently reported for $NiFe_2O_4$ and $MgFe_2O_4$ spinel ferrites [20,21]. In this way, the relatively high magnetization measured for this orthoferrite can be attributed to a combination of both mechanochemical and doping effects.

XRD patterns for as-milled and calcined ($T = 600, 800$ and $1000^\circ C$) YML3 samples are shown in Figure 3. A continuous narrowing of the $Y_{0.5}La_{0.5}FeO_3$ peaks at higher temperatures is observed, which is due to the increase in the crystallinity and grain size of the orthoferrite obtained during the milling. Crystallite size, determined with Scherrer equation, changes from 17 to 26 nm between 600 and $1000^\circ C$ respectively. At $1000^\circ C$ small peaks corresponding to $Y_3Fe_5O_{12}$ are also detected. This mixed oxide with garnet structure is a common impurity in the synthesis of $YFeO_3$, because of its high thermodynamic stability [22].

Lattice parameters of $Y_{0.5}La_{0.5}FeO_3$ obtained from YLM3h heated at $1000^\circ C$ are summarized in Table 1. These values are presented together with the corresponding lattice parameters of the parent compounds, $LaFeO_3$ and $YFeO_3$, which were taken from powder diffraction files database [23]. A comparison between the three orthorhombic structures reveals that doping with Y^{3+} produces a significant decrease of the unit cell volume, which is an expectable effect due to the smaller size of this cation with respect to La^{3+} . However, the lattice

contraction is not isotropic: parameters b and c undergo a pronounced decrease whereas a shows a slight increase, indicating a distortion of the lattice geometry as yttrium content grows. This result agrees with a previous report [24].

Table 1. Lattice parameters for the orthorhombic ferrites LaFeO_3 , $\text{Y}_{0.5}\text{La}_{0.5}\text{FeO}_3$ and YFeO_3 .

	a (Å)	b (Å)	c (Å)
LaFeO_3	5.5679	7.8627	5.5845
$\text{Y}_{0.5}\text{La}_{0.5}\text{FeO}_3$	5.5704	7.8148	5.5063
YFeO_3	5.5934	7.6538	5.2837

In order to determine the effect of yttrium doping on the magnetic response of lanthanum orthoferrite, its M vs H dependence was compared with that of a LaFeO_3 sample mechanosynthesized in a similar way [14]. In Figure 4, the magnetic loops of both samples are compared. The value of M_s obtained for the yttrium-doped compound is significantly higher than that exhibited by the undoped oxide. This effect can be explained by taking into account the distortion of the lattice produced by the replacement of La^{3+} by Y^{3+} , besides the defects introduced by the mechanochemical treatment itself. Furthermore, the reduction of the cell volume can be graphically noticed by the relative shift of XRD peaks, shown in the inset of the figure.

Figure 5 displays the magnetic measurements for samples YML3h (as-milled and heated at 600, 800 and 1000°C). A monotonic decrease of M_s and H_c as temperature increases up to 800°C is observed. Thermal treatment allows the relaxation and elimination of the crystalline defects accumulated during the mechanical treatment, yielding a much more ordered structure with a spin arrangement close to an antiparallel configuration. However, heating at 1000°C leads to an increase in M_s together with a change in the shape of the hysteresis loop. This behavior is related to the presence of $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (also detected by XRD, Fig. 3), which is a ferrimagnetic oxide with an M_s of approximately 26 emu/g [25]. Assuming that in this sample the contribution of $\text{Y}_{0.5}\text{La}_{0.5}\text{FeO}_3$ to M_s is negligible, the garnet content is estimated to be about 5%.

CONCLUSIONS

Nanocrystalline orthoferrite $\text{Y}_{0.5}\text{La}_{0.5}\text{FeO}_3$ was synthesized at room temperature by very short mechanochemical treatments of La_2O_3 - Y_2O_3 - Fe_3O_4 powder mixtures. Magnetic

measurements revealed that this phase has a relatively high magnetization, suggesting that the mechanochemical activation induces the formation of a distorted crystal structure with a non-collinear spin ordering. The comparison with mechanosynthesized LaFeO_3 proves that structural distortions provoked by both doping and mechanochemistry significantly increase the magnetic moment of these essentially antiferromagnetic compounds. The structural defects accumulated during the milling were released by heating the solid, leading to a nearly antiferromagnetic state. At 1000°C a relatively small amount of $\text{Y}_3\text{Fe}_5\text{O}_{12}$ was detected.

ACKNOWLEDGEMENTS

We wish to thank CONICET, CIC, ANPCyT, UNMdP and UNC for financial support.

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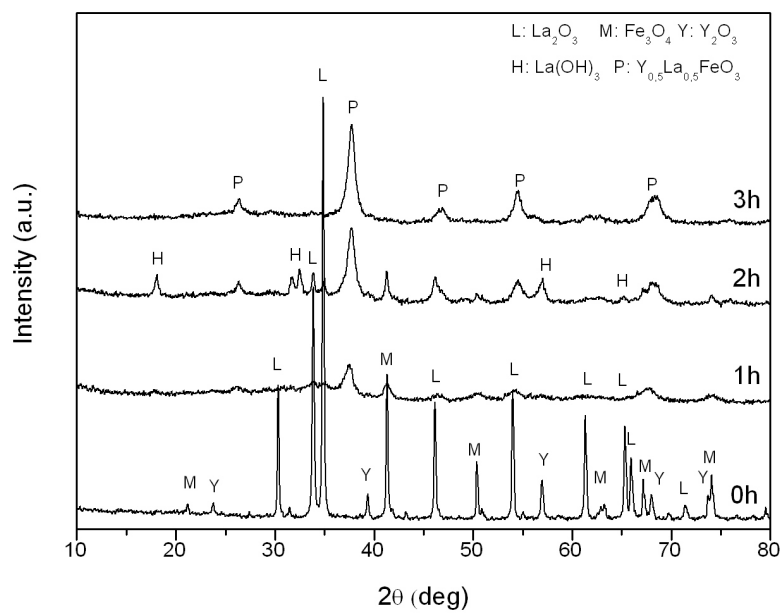


Figure 1. XRD patterns of samples mechanically activated for several times.

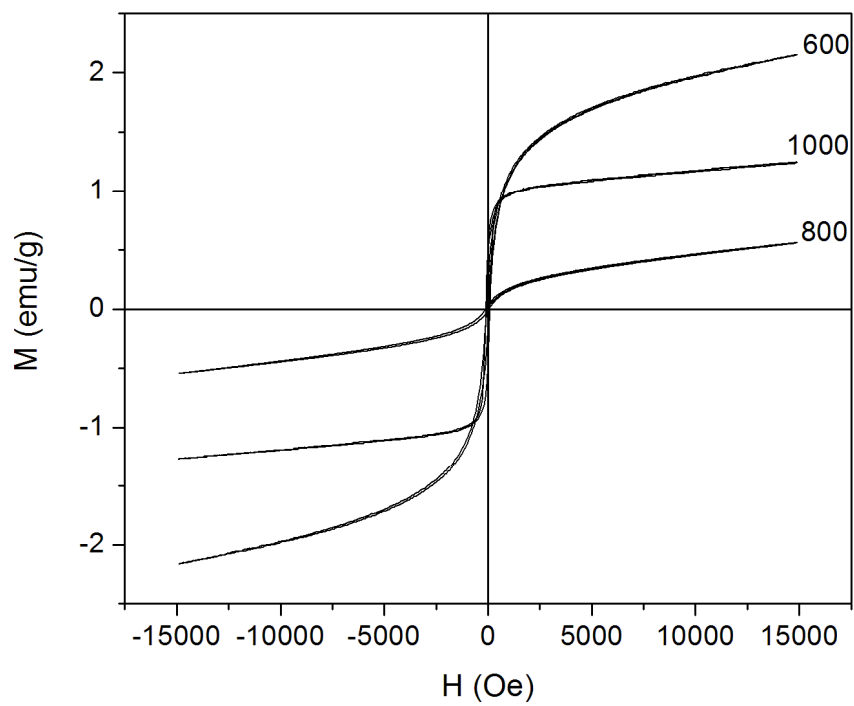


Figure 2. M vs H curves for the series of activated samples. The inset shows the variation of M_s and H_c with activation time.

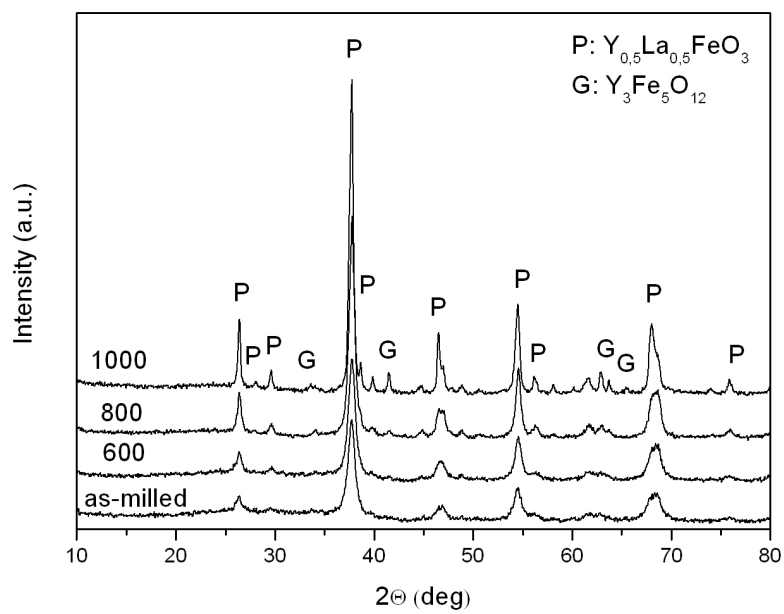


Figure 3. XRD patterns of as-milled and thermally treated sample YML3h. Heating temperatures are indicated on each curve.

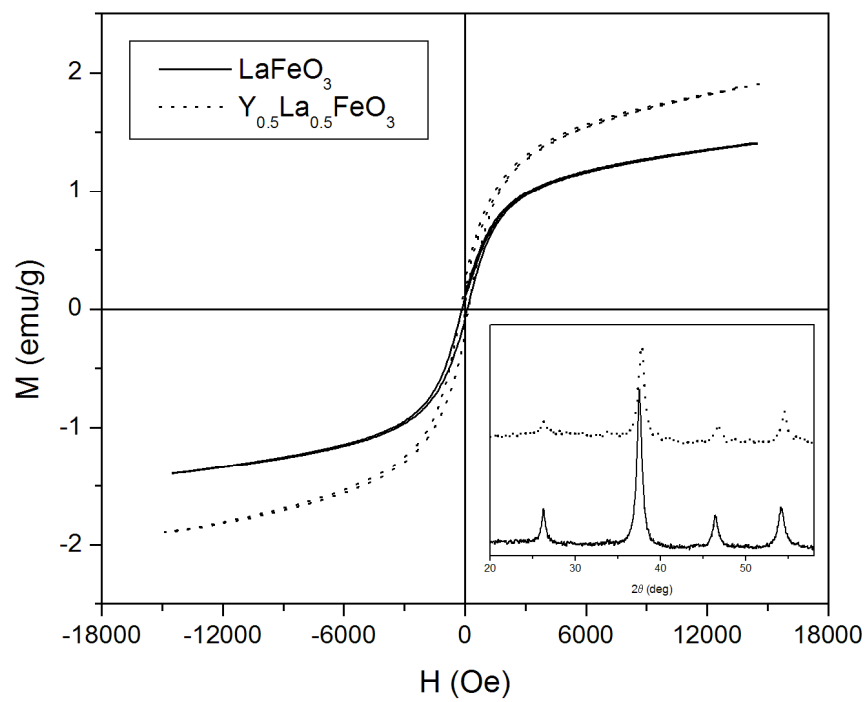


Figure 4. M vs H curves for mechanosynthesized $\text{Y}_{0.5}\text{La}_{0.5}\text{FeO}_3$ and LaFeO_3 . The inset shows the shift of XRD peaks with yttrium doping.

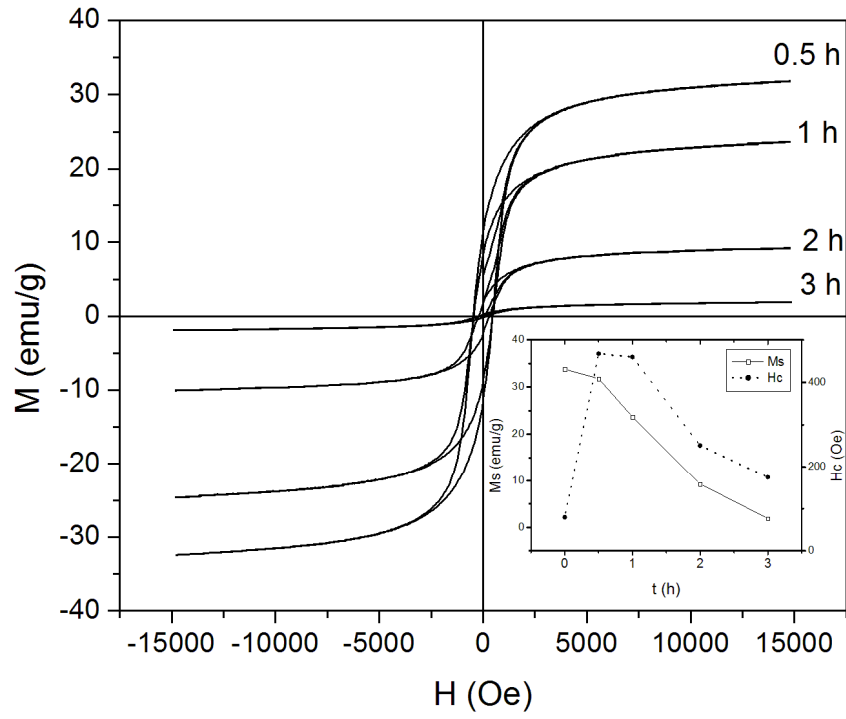


Figure 5. M vs H curves for as-milled and thermally treated sample YML3h. Heating temperatures are indicated on each curve.