Hyperfine and magnetic properties of a $Y_xLa_{1-x}FeO_3$ series $(0 \leq x \leq 1)$

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ABSTRACT

A series of orthoferrites $Y_xLa_{1-x}FeO_3$ in the entire range of composition was synthesized at room temperature by mechanochemical activation of oxide mixtures. Phase composition, structure and microstructure of the obtained powder materials were characterized by X-ray diffraction and field-emission scanning electron microscopy. Hyperfine interactions and magnetic properties were determined by Mössbauer spectroscopy, SQUID and vibrating sample magnetometry. Two magnetic contributions could be identified in the series of materials: a paramagnetic state, associated with a fraction of the smallest particles and a ferromagnetic state, attributed to the larger particles. The results showed that the relative proportion of both contributions is very dependent on x, the Y content of samples. From M vs T measurements, it was possible to estimate the blocking temperature distribution for the end members of the series. Annealing of samples produced the elimination of the superparamagnetic behavior and the formation of $Y_3Fe_5O_{12}$ impurities.

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1. Introduction

Orthoferrites with general formula $AFeO_3$ are a prominent family of inorganic compounds, because of the plethora of properties and applications that they often exhibit. In most cases, they crystallize in a perovskite-type structure, with corner-sharing FeO_6 octahedra and A cations occupying the center of a cube (generally with an orthorhombic or rhombohedral distortion) [1]. From a technological point of view, materials based on ortho-ferrites are interesting because they can be used in a wide range of applications: sensors, catalysts, solid oxide fuel cells, etc [2–4]. Their functional properties (electrical conductivity, magnetization, catalytic activity) are very dependent on the structure, which can be significantly modified through the incorporation of cations with different sizes and charges [5–7]. Frequently, the size of cation A determines the structure adopted by orthoferrites, being ideal perovskite structures (cubic) or distorted ones (tetragonal, orthorhombic, rhombohedral). The distortion is produced by the cooperative tilting of FeO_6 octahedra around their own axes [8]. In order to estimate the distortion degree, the tolerance factor of Goldschmidt (t) [9] can be calculated using adequate values of ionic radii (frequently radii provided by Shannon [10]). When $t = 1$,

orthoferrites crystallize in a cubic structure, and when t decreases (not lower than 0.75) the lattice has an orthorhombic or rhombohedral symmetry.

$LaFeO_3$ and $YFeO_3$ are two perovskite-type ferrites, whose stable structures at room temperature have an orthorhombic crystal symmetry. The first one has in fact a quasi-tetragonal structure (lattice parameters a and b are almost identical) whereas the second one presents a lower symmetry, because of the less similarity between a and b. The magnetic structure of these compounds can be described as a two-sublattice system formed by FeO_6 octahedra strongly antiferromagnetically coupled and slightly canted, producing a net magnetic moment perpendicular to the antiferromagnetic axis. The canting angle is very small (milliradians) and depends on the A-cation size [11,12]. These features and the extraordinary domain-wall motion of these compounds make them suitable for magneto-optical devices, such as switches and sensors [13–15].

A wide and diverse variety of preparative routes has been used to produce $LaFeO_3$ and $YFeO_3$. Among them, conventional solid-state method, combustion synthesis, sol–gel, hydrothermal synthesis and co-precipitation technique have been mostly used [16–19]. Generally, micro or nanoparticles of $LaFeO_3$ can be easily obtained free of impurities. By contrast, preparation of $YFeO_3$ is often problematic, because the formation of the garnet $Y_3Fe_5O_{12}$ (YIG) competes in the reaction [20,21]. Other methods have demonstrated to be more efficient than solid-state reactions to

avoid or minimize this limitation [22–24]. Anyhow, Cristóbal et al. have reported a mechanically assisted solid-state route for producing both compounds, pure and nanocrystalline [25,26]. High-energy ball-milling of oxide precursors is a convenient way to favor the kinetics of solid-state reactions, commonly retarded by very slow ionic diffusion rates. Some of the operative advantages of this synthesis method are the possibility of obtaining relatively large amounts of powders, the occurrence of solid-state reactions at room temperature and the absence of organic solvents throughout the process [27–29]. On the other hand, the incorporation of large amounts of structural defects during the milling produces significant changes in the properties which are dependent on structural ordering, such as the magnetic ones [30–32]. In previous reports, we have shown the link between magnetic behavior and the alteration of crystal ordering provoked by the mechanochemical action in the synthesis of $LaFeO_3$, pure and modified with Y [26]. However, the extreme complexity of the system requires a deeper insight into the magnetic interactions, in order to properly understand the observed responses. Here we present a detailed investigation of hyperfine and magnetic properties of the series $Y_xLa_{1-x}FeO_3$ ($0 \leq x \leq 1$), synthesized by high-energy ball milling.

2. Experimental

Powder mixtures of Fe_3O_4 (a magnetite concentrate ore, 97.5%), La_2O_3 and Y_2O_3 (commercial reagents, 99.9%) with different molar ratio were prepared and mechanochemically activated in a Fritsch Pulverissette 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. Oxygen supply was assured by periodically opening the vials, at the time that small portions of powder were withdrawn in order to follow the evolution of the activation process. Five compositions with yttrium contents (x in the formula $Y_xLa_{1-x}FeO_3$) ranging between 0 and 1 were ball-milled for 3 h. The activated powders were then thermally treated at 1000 °C for 30 min in air atmosphere. The series of as-milled samples was named YLM-x while the calcined samples were labeled YLM-x-1000, being x the Y content.

Fig. 1. XRD patterns for samples YML-x and YML-x-1000 ($x = 0$, 0.5 and 1) as-milled and heated at 1000 °C. Indexed peaks belong to $Y_xLa_{1-x}FeO_3$; peaks marked with * belong to YIG phase. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.1. Characterization

The structure of crystalline phases was analyzed by X-ray diffraction (XRD) using a Philips PW 1830/40 diffractometer at 40 kV and 30 mA, with CoKα radiation ($\lambda = 0.17890$ nm) and Fe filter.

Magnetization (M) at room temperature as a function of applied field (H) was measured using a Lakeshore 7300 vibrating sample magnetometer. Magnetic loops between +15 and −15 kOe were registered. M vs T measurements were performed in a SQUID magnetometer (Quantum Design) under a zero-field cooling (ZFC)/field cooling (FC) regime.

Sample microstructures were studied by field emission gun scanning electron microscopy (FEG-SEM), using a Zeiss Supra40 electron microscope.

Mössbauer spectra were taken at room temperature (RT) and 20 K in a conventional constant acceleration spectrometer in transmission geometry with a $^{57}Co/Rh$ source. The absorber thickness was chosen to be the optimum according to the Long et al. criterion [33]. Least-squares fitting of the spectra was performed by using the Normos program [34]. Isomer shift (IS) values are given relative to that of α-Fe at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of the series of activated and calcined samples for $x = 0$, 0.5 and 1. The completion of the reaction is confirmed by the absence of reactants' peaks and the formation of the corresponding orthoferrite.

As x increases, additional peaks corresponding to $Y_xLa_{1-x}FeO_3$ appear as a consequence of the loss of crystalline symmetry. Also, a shifting to towards higher 2θ values with Y content is observed because of the smaller size of Y^{3+} cation in comparison with La^{3+} cation. [26]. The peaks' profile for the as-milled samples denotes a very small crystallite size, which grows after heating at 1000 °C. An estimation of crystallite size using the Scherrer equation gives 10 nm for the unheated samples and 50 nm for heated powders, approximately. The XRD pattern of sample YML-1–1000 shows small peaks (indicated with * in Fig. 1) corresponding to a secondary phase (YIG), a very common impurity in the synthesis of $YFeO_3$ [20,21].

Room temperature (RT) Mössbauer spectra for the as milled samples – in the whole composition range – were fitted to a doublet and to a hyperfine field distribution, reflecting a particle size distribution. Fig. 2 (left column) shows a comparison between the different spectra. An evident evolution is observed as Y content increases; the doublet grows monotonically in a linear way. Table 1 exhibits the hyperfine parameters obtained by the fitting procedure with their relative contributed areas, which are proportional to the concentration of the corresponding Fe species.

The hyperfine field distribution parameters are typical for Fe^{3+} in octahedral coordination, in accordance to the orthoferrite phase structure and as Y content increases its medium value, B_{hf}, diminishes (Fig. 2 and Table 1). This may be the consequence of a change in the super-transferred hyperfine field, arising from distortions in the Fe–O–Fe bond lengths and angles. These distortions are more likely in the smaller particles because surface effects are intensified.

The maxima of the magnetic hyperfine field distribution for samples YLM-0 (~51 T) and YLM-1 (~48 T) respectively are smaller than those of the bulk values reported in literature [35,36], suggesting small particle sizes.

In order to clarify the presence of the doublet, Mössbauer spectra were also taken at 20 K. As an example, Fig. 3 shows the spectra for sample YLM-1 at RT (a) and 20 K (b). At RT, part of the spectrum is magnetically sp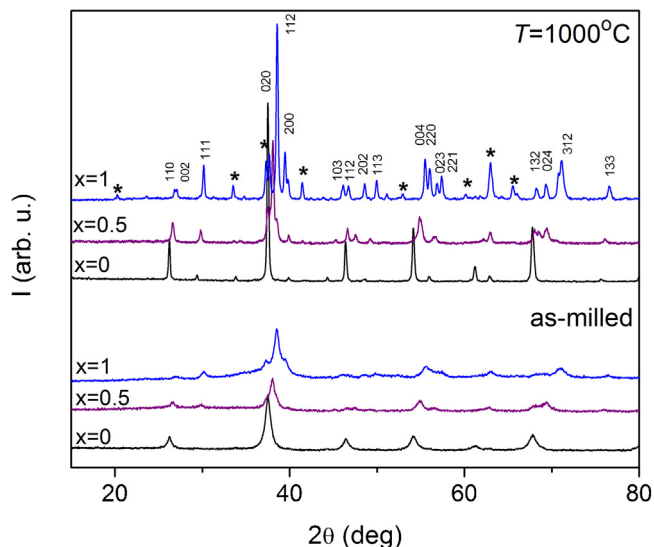lit and as temperature is reduced to