Structural magnetic and Mössbauer study of ^{57}Fe doped La$_{2/3}$Ca$_{1/3}$Mn$_{1-x}$Fe$_x$O$_3$ (0≤x≤0.1) manganites

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Abstract. We have studied the effect of ^{57}Fe substitution on structural and magnetic properties of La$_{2/3}$Ca$_{1/3}$Mn$_{1-x}$Fe$_x$O$_3$ (LCMFO; x=0, 5 and 10%) manganites. The powders were prepared by the solid state reaction method, and the final products were characterized by X-Ray Diffraction (XRD), Mössbauer Spectrometry and Magnetic Measurements. Only one single phase corresponding to the manganite phase was detected without the presence of impurities or iron phases. The hyperfine parameters of Mössbauer spectra (MS), taken at different temperatures for the doped samples, reveal the only presence of Fe^{3+} ions in octahedral coordination. At low temperatures, the MS spectra were fitted with a model of three components associated to three magnetic phases of iron (ferromagnetic and paramagnetic states). These ordered and not ordered magnetic phases are related to the effects of grain size distribution in LCMFO samples. Finally, significant changes were observed in the saturation magnetization, Curie temperature and coercivity field with increasing of iron doping level.

1. Introduction

Colossal magnetoresistance (CMR) in manganites has generated a rise on studying these materials because of both interesting fundamental properties and potential device applicability. In particular, the manganite La$_{1-x}$A$_x$MnO$_3$ (A=Ca, Sr, Ba, Pb) presents a remarkably complicated phase diagram as the relative concentration of Mn^{3+} and Mn^{4+} changes. Ferromagnetic order is due to double exchange (DE), via Mn^{3+}–O^{2-}–Mn^{4+}, whereby ferromagnetic (FM) interactions between localized spins are mediated by hopping of itinerant spins [1]. In order to study the influence of Fe doping on the electrical, structural and magnetic properties of manganites, early studies have shown the direct replacement of Mn^{3+} by Fe^{3+}, considering their similar ionic sizes. Mössbauer spectroscopy (MS) is an important technique to provide information about the nature of the local induced magnetic effects, small changes in the local electronic and vibrational state of ^{57}Fe via hyperfine interactions. In this context, we thought it is interesting and useful to show the results of the effects of varying the content of ^{57}Fe on the structural and magnetic properties in La$_{2/3}$Ca$_{1/3}$Mn$_{1-x}$Fe$_x$O$_3$ (0≤x≤0.10) manganite powder samples, prepared by solid state reaction method.

2. Experimental

Powder samples of La$_{2/3}$Ca$_{1/3}$Mn$_{1-x}$Fe$_x$O$_3$ with x=0, 0.05 and 0.10 nominal composition were prepared by the solid state reaction method with high purity (>99.9%) precursors of La$_2$O$_3$ (Lanthanum oxide), MnO$_2$ (Manganese dioxide), CaCO$_3$ (Calcium carbonate), and α-Fe$_2$O$_3$ (Hematite) 95.06% enriched with ^{57}Fe. The powders of these oxides were mixed and heated in several stages with temperatures

among 900°C and 1300°C to obtain $La_{2/3}Ca_{1/3}MnO_3$ (LCMO), $La_{2/3}Ca_{1/3}Mn_{0.95}Fe_{0.05}O_3$ (LCMFO-5%), and $La_{2/3}Ca_{1/3}Mn_{0.90}Fe_{0.10}O_3$ (LCMFO-10%) powders. The samples were analysed by XRD (x-ray diffraction) using a Bruker Advance 8.0 with a Cu (Kα) source, in Bragg-Brentano geometry. The data were collected in the range 20–80° in 2θ with steps of 0.013°, and the patterns were fitted by employing the Rietveld refinement analysis implemented in the FULLPROF-SUITE program. The absorption ^{57}Fe Mössbauer spectra were recorded in a conventional Mössbauer spectrometer with a ^{57}Co (Rh) source, while the absorbers were collected through a cryostat at variable temperatures range from 7 to 300K. These spectra were analysed using the NORMOS program to obtain the hyperfine parameters. Magnetic measurements, zero field cooling (ZFC) and field cooling (FC) curves, and hysteresis loops (at 7, 50, 100, 200 and 300K) were performed via vibrating-sample magnetometer technique (VSM) with the physical properties measurement system (PPMS, Quantum Design). The ordering temperature (T_C) was determined from dM/dT derivative of the ZFC curves. The difference between FC and ZFC curves was used to estimate the irreversibility temperature (T_I).

3. Results and discussion

The structural parameters of all samples were obtained by fitting with the Rietveld refinement method the XRD patterns (see Figure 1), assuming the perovskite structure (orthorhombic Pnma-(62) space group). The obtained lattice parameters and cell volumes are shown in Table 1. Peaks of other phases such as secondary oxides or impurities were not detected. Both the lattice parameters and the cell volumes slightly increase with the Fe doping. These results indicate that due to both Fe^{3+} and Mn^{3+} have almost identical ionic radii, thus, the crystalline structure is not modified by Fe doping in our concentrations. Similar results were reported by Cai [2] and Ogale [3] et al. Additionally we estimated the average crystallite size about of 305, 328, and 340nm, for LCMO, LCMFO-5% and LCMFO-10%, respectively. For this, the patterns were analysed by using MAUD program, which combines the Rietveld method and a Fourier transform analysis.
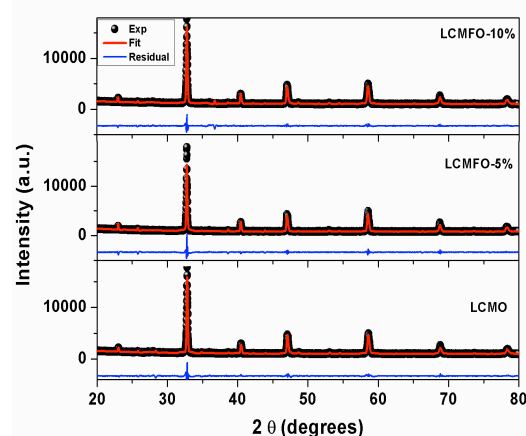

Figure 1. XRD patterns fitted with Rietveld refinement. Continuous lines represent the fit.

Table 1. Crystallographic and magnetic parameters of LCMO, LCMFO-5% and LCMFO-10% samples. a, b, and c are the cell parameters, V the cell volume, T_C and T_I are the Curie and irreversibility temperature, respectively.

Sample	a (Å)	b (Å)	c (Å)	V (Å)^3	T_C (K)	T_I (K)
LCMO	5.449	7.695	5.464	229.1	271	260
LCMFO 5%	5.460	7.706	5.466	230.0	179	175
LCMFO 10%	5.461	7.707	5.467	230.1	160	136

The temperature evolution of Mössbauer spectra (MS) for the LCMFO-5% and LCMFO-10% samples recorded at temperatures between 7 and 300K are shown in Figure 2 and Figure 3, respectively. At 300K, the spectra were fitted considering a paramagnetic doublet (D2) [4]. The values of isomer shift are typical of Fe^{3+} ions in octahedral coordination, while the small quadrupole splittings of the samples indicate a slight distortion of the octahedron. As temperature is further reduced, we detected a six-line spectrum (S1) with hyperfine parameters that corroborate the presence of Fe^{3+} ions. For this fitting model it was assumed Lorentzian line shape with the same line width, isomer shift and quadrupole interaction, based on a discrete distribution model used of Simopoulos et al [5]. The obtained values of quadrupole splitting might be explained by a possible structural transformation of the perovskite matrix (Mn site), in according to reports made by other authors [6,7]. In the

temperatures intermediate range between 150 and 100K, we found the same behaviour of the distributed magnetic sextet with asymmetric line broadenings; it was attributed to early manifestation of magnetic ordering with decreasing temperature. At low temperatures, the fits were obtained by introducing an additional crystalline sextet (S2), with hyperfine parameters associated again to the presence of Fe^{3+}. At 7K the MS displays a well-defined crystalline component, a broad distributed magnetic sextet, which corresponds to smaller effective hyperfine magnetic fields, and a paramagnetic doublet. This validates the presence of three different iron sites leading to a moderate distribution in the hyperfine magnetic field (see Figure 4). Figure 5 shows M(T) in both ZFC and FC modes for applied external magnetic field of 500 Oe. The obtained values of T_C were 271, 179 and 160K, for LCMO, LCMFO-5% and LCMFO-10%, respectively. We found that paramagnetic contribution remains in the spectra below T_C and decreases with the diminution of the temperature. The presence of paramagnetic fractions PM in our Mössbauer spectra could be associated to a dynamic phase separation, i.e. coexistence of small ferromagnetic FM domains (clusters) undergoing superparamagnetic like relaxation and small PM insulating clusters in the vicinity of T_C.

From the estimated average crystallite size for our samples (around 300nm), the temperature evolution of the MS cannot be attributed to classical superparamagnetism [7]. In the doped samples, the main effect of the substitution of a Fe by a Mn site is the reduction of both T_C and saturation magnetization M_S regarding to the undoped sample. The M_S estimated at 7K of the hysteresis curves (not shown) were 88.3, 76.8 and 57.4emu/g for the LCMO, LCMFO-5% and LCMFO-10% samples, respectively. Furthermore, a broader ferromagnetic-paramagnetic FM-PM transition in the M(T) curves (see Figure 5) with the Fe concentration were observed. Following the results of X. Wang et al. [8] we could attribute this broadening to the effect of antiferromagnetic (AF) couplings between Fe and its neighbors, which causes a weaker magnetic interaction between Mn-Mn, in according to our Mössbauer and magnetic measurements.
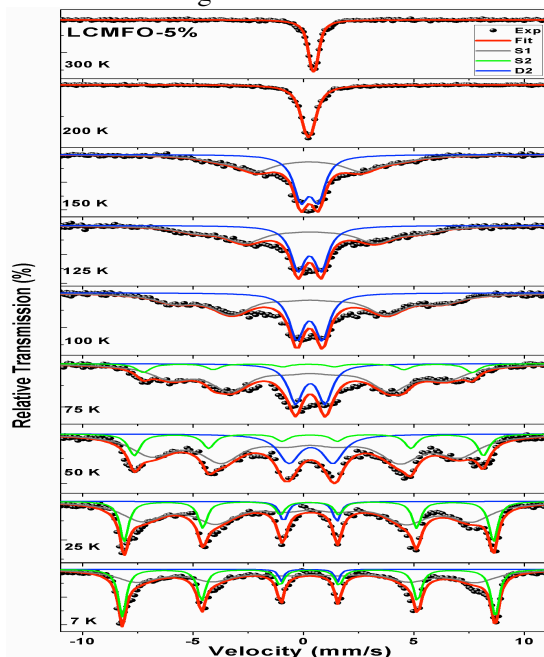

Figure 2. MS of LCMFO-5% at temperatures from 7 to 300K. Closed circles are experimental data, colour lines are different components (S1, S2 and D2) and red line is the fit.
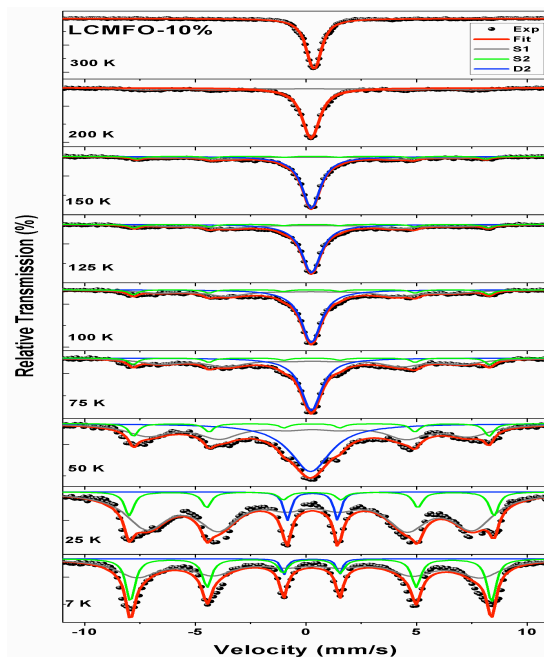
Figure 3. MS of LCMFO-10% at temperatures from 7 to 300K. Closed circles are experimental data, colour lines are different components (S1, S2 and D2) and red line is the fit.
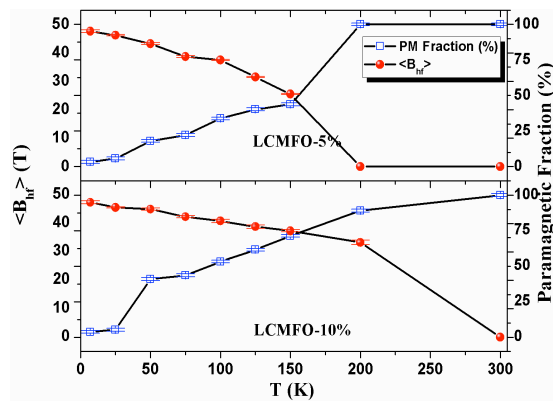
Figure 4. Average hyperfine magnetic field $<B_{hf}>$ and paramagnetic fraction versus temperature for LCMFO-5% and LCMFO-10% samples.
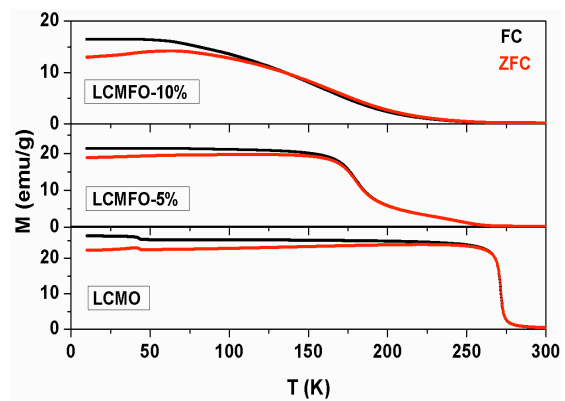
Figure 5. Magnetization M(T) versus temperature (ZFC and FC modes) in a 500 Oe field for LCMO, LCMFO-5% and LCMFO-10% samples.

4. Conclusions

Fe^{3+} ions not only introduce an important antiferromagnetic superexchange interaction, but also lead to a substantial decrease in the double exchange mechanism. The possible explanation for the temperature evolution of the Mössbauer spectra and the persistent paramagnetic contribution in our system is the presence of ferromagnetic clusters with size distribution. These clusters with small sizes display paramagnetic behaviour, caused by the fast fluctuation of the magnetic moment at a certain temperature and as the temperature decreases, the fluctuation decreases and the cluster displays magnetic hyperfine splitting. Finally, the distortion of the octahedron according to the Fe by Mn substitution could result in a tilting of the magnetic moments; this may explain the decrease in the Curie temperature, consistent with Mössbauer and magnetic measurements.

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