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Analysis of magnetic and structural properties in $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ ferromagnetic particles under the influence of mechanical ball milling effect

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Abstract. We have investigated the magnetic, structural and morphological properties of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (LSMO-40) manganite particles, synthesized by solid state reaction method. The resulting LSMO-40 powders were milled in air atmosphere during 3, 6 and 12 hours, by using a planetary ball milling. Samples obtained were characterized by X-ray diffraction, scanning electron microscopy - SEM and magnetization measurements as a function of temperature and magnetic field. A Rietveld analysis was carried on each XRD pattern, and was observed a reduction in crystallite average size (D_v) with increased ball milling time, t_M . This is associated with a decrease in particle size. A characteristic rhombohedral crystal structure for the LSMO-40 phase was identified (space group R3C), independent of the milling time of the powders. However, from SEM microstructure was observed more homogeneity in the grain distribution by milling process. The results of magnetic characterization, showed that samples with higher t_M (smaller grain size), presented the lowest value of the saturation magnetization, which is attributed to surface effects that induce magnetically disordered states with decreasing particle sizes. This magnetic anisotropy surface is evidenced also on the changes of coercive fields, H_C , measured at low temperatures, which increased with increasing t_M .

1. Introduction

Since the discovery of Colossal Magnetoresistance (CMR) phenomenon, which is caused by double exchange mechanism DE [1], in $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ (A= Sr, Ca, Ba, etc) named manganites, it has been found new and exciting properties for potential applications in different areas [2, 3]. These doped manganites, which possess a perovskite structure, show a variety of phases depending of stoichiometric structure [4]. Particularly, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) manganite has been focus of important attention due besides of CMR effect, to its high Curie temperature (T_c), conduction by spin-polarized and close lattice parameter with others compounds, in a range of x concentration [5]. The physical properties of this systems are sensitive to size effect depending of the fabrication, in single crystal, thin films (lattice strain, interfaces effects) or powders (core-shell effects) [6-8]. In the case of particles at nanosize scale of LSMO, recently they have been much studied because of grain boundaries effects, which have shown significant differences in their physical properties respect to the bulk material, having very important applications. A reduction of grain size was found to influence the magnetization and coercivity in these compounds. Among the models proposed for describe these



particular behaviours, has been found that the structural disorder near to grain boundary, affects the DE mechanism due to its sensitivity to changes in the stoichiometric composition, vacancies, dislocations, etc. This produces magnetically disorder states, in the surface of the grains. In this work we report a structural and magnetic analysis of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (LSMO-40) powders, obtained by solid state reaction method, and subjected to mechanical ball milling. Models based on the contribution of the grain surface on the magnetization and coercivity, and the dependence of the magnetic properties with the particle size, is discussed.

2. Experimental

In this work, a pure phase of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (LSMO-40) ferromagnetic manganite was obtained by solid state reaction method. The phase was obtained from the mixture of high purity precursors, synthesized according to the appropriated stoichiometric molar amounts. In order to reduce the particle size of the LSMO-40 sample, the powder was subjected to mechanical milling process in air atmosphere, by using a planetary ball milling Fritsch PULVERISETTE 5. For this study, were established three different milling times: 3, 6 and 12 hours, with a ball-to-powder ratio of 20:1 (using stainless-steel balls), for counting with a set of 4 samples (including unground sample – Non-Milling (NM)) of this manganite. The crystallographic structure of the powders was performed by X ray diffraction (XRD), with a Cu-K α radiation source. All XRD patterns were fitted by using the Rietveld refinement analysis in order to obtain structural parameters, including the average crystallite size for each milling time, t_M . Finally, magnetic measurements were performed via vibrating-sample magnetometer (VSM) with the physical properties measurement system (PPMS, Quantum Design). All measurements were taken by using a 40-Hz vibration frequency for the detection coil with 2-mm. Magnetization curves as a function of the temperature M (T), were measured varying temperature from 5 to 375 K, for both Field Cooling (FC) and Zero Field Cooling (ZFC), with an external applied magnetic field of 500 Oe. Magnetization hysteresis loops M (H), were measured in the ranges of applied magnetic field from -5 kOe to 5 kOe.

3. Results and discussion

The X-ray diffraction is used to verify the crystal structure of the samples. In figure 1 (a) shows the XRD diffraction data and the Rietveld refinement, for all milling time of LSMO-40 samples. It is observed a good correspondence between the experimental data and the fit, which showed a single crystallographic phase, corresponding to the rhombohedral structure that belongs to space group R3C. This structural phase, characteristic for this manganite [9], is present for all t_M , including the sample without grinding, indicating that the process of synthesis for this concentration crystallizes in a single phase, which is stable under the grinding conditions defined in this study. Average crystallite size values have been extracted from Rietveld refinement in the maximum XRD peak, for each t_M , see figure 1 (b). It is noted that the crystallite size decreases rapidly from 48 nm for non-milled (NM) sample, to 26 nm for 3 hours milled sample, and then the rate decreases with increasing milling time. An average crystallite size of around 21 nm was obtained for 12 hours of milling, indicating that for this time, is more difficult obtain smaller particle size by ball milling method.

Figure 2 shows the zero field cooling (ZFC) and field cooling (FC) curves of magnetization as a function of temperature for NM sample (a) and for the sample subjected to 12 hours of milling (b), measured during warming up from 5 to 375 K, in 500 Oe after cooling in zero field and applied field of 1 kOe, respectively. M (T) shows the ferromagnetic-paramagnetic (FM-PM) transition typical for this concentration. We observed a difference between ZFC and FC curves, for both NM as for 12 h milled. The curves coincide at temperatures above 250 K and become zero around the Curie critical temperature T_C , where the FM-PM transition occurs. It is worth noting that T_C is similar for both samples approximately at 370 K, and similar to that reported for LSMO-40 in bulk. However, the magnetization at low temperature for non-milled sample, shows that FC at 5 K is around of 0.10 (emu) higher than ZFC, as it is observed in figure 2 (a), and becomes about two times larger than ZFC for the

sample with 12 hours of milling, figure 2 (b). This indicates that FC and ZFC curves show a magnetic irreversibility, which manifests below to approximately 250 K, and increases with the milling time.

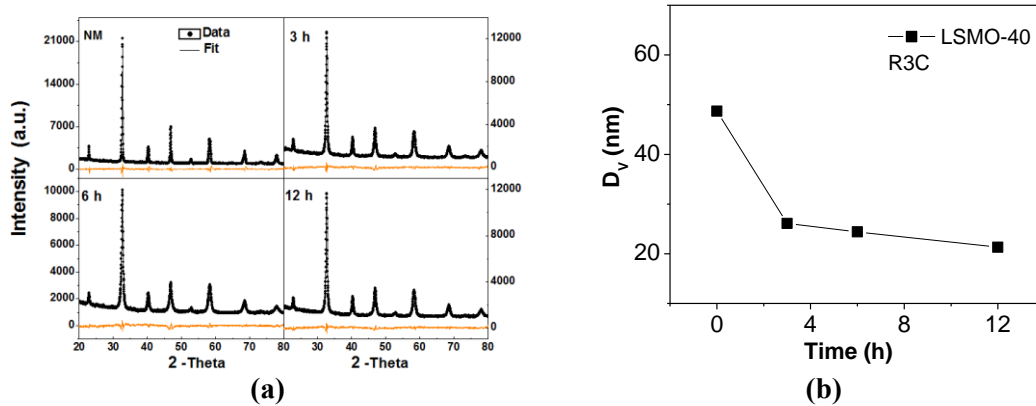


Figure 1. (a) Experimental and calculated XRD patterns with Rietveld refinement for LSMO-40 with different milling time (NM is the sample without milling). (b) Average crystallite size (D_v) as a function of t_M .

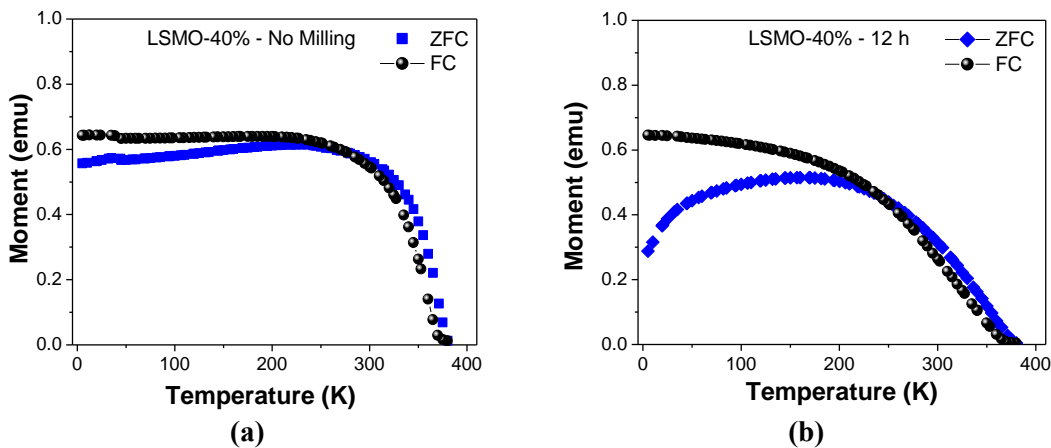


Figure 2. ZFC and FC magnetization of LSMO as a function of temperature for no milling, NM (a) and for milling time of 12 hours (b).

This behavior can also be attributed to the presence of surface inhomogeneities related with a spin disorder or magnetic anisotropy, which increases when the grain size decreases. Above 250 K the thermal fluctuation balances the anisotropy energy, and in this way both curves coincide around of transition. However, it is observed a broadening of the magnetic transition when increase the t_M , compared with a more abrupt transition in the NM sample, where the behavior is comparable with that of bulk LSMO and the size effects seems that are not present. As to the magnetization as a function of applied magnetic fields $M(H)$, studied in a range of ± 5 kOe, at 5 and 300 K for NM and 12 h samples, are shown in figure 3 (a). From the data one can find that the saturation magnetization varies slightly with the milling time, taken at the same temperature value, but the difference is most evident at low temperature compared with the values at room temperature, around of 0.75 emu for both samples, shown in the figure 3 (a). Nevertheless, the thermal dependence of coercivity decreases with increase of temperature for small grain. The coercive field H_C , measured at 5 K is larger than that value corresponding to 300 K for the sample with 12 h of milling. Figure 3 (b) shows the H_C values for all milling time, taken to 5 and 300 K.

In general, there is an increase in the H_C values with t_M at 5 K, and it became one order of magnitude higher (for 12 h sample) than the value measured in the NM sample. However, for the H_C values at room temperature, the coercivity remain almost constant and there is no a significant dependence with t_M . Such behavior is related with disordered states at the surface level, which influence the magnetic properties of the particles when their size is diminished. In this way, a reduction in the magnetization and increase of coercivity, can be related with a decrease in the spin order in the surface due to size effects that results in a suppression of the DE mechanism, characteristic of these systems.

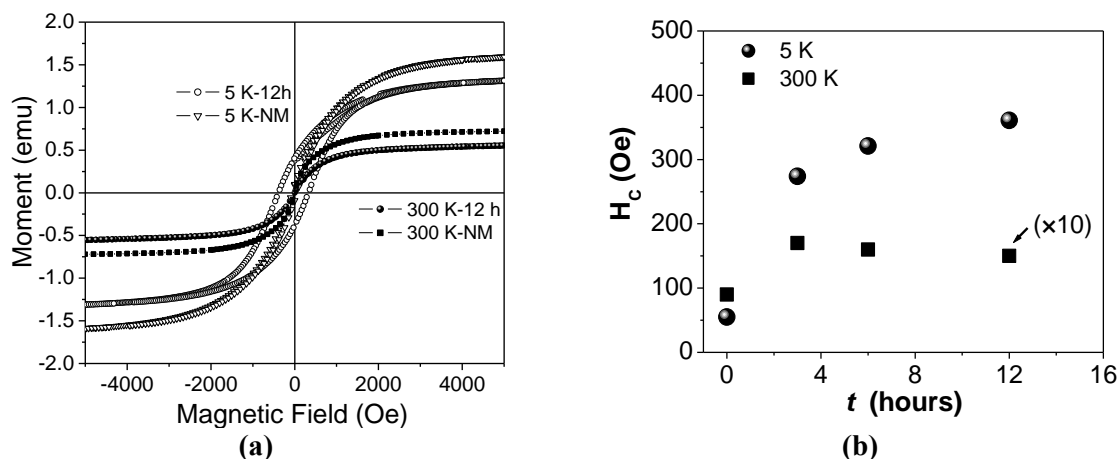


Figure 3. (a) Hysteresis loops for NM and 12 h samples, measured at 5 and 300 K. (b) Coercive fields extracted from $M(H)$ for all milling time, at 5 and 300 K.

4. Conclusions

In summary, the results presented in this work, showed the relation of structural and magnetic properties with decreasing of grain size, of powders of manganite $La_{0.6}Sr_{0.4}MnO_3$ (LSMO-40), subjected to different milling time. The Rietveld analysis showed a single phase present in NM and all samples milled. A decreased average crystallite size values with t_M was found. Samples studied in this work showed dependence with t_M , which was evidenced by decreasing magnetization and increased coercive fields (measured at low temperature). This behaviour is attributed predominantly to size effects which results in a magnetic anisotropy at surface level that can affect the DE mechanism.

Acknowledgements

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