Grain Size Reduction Effect on Structural and Magnetic Properties in La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.3$ y $0.4$) by Mechanical Ball Milling

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Abstract. We have investigated the magnetic, structural and morphological properties of ferromagnetic phases of manganite La$_{1-x}$Sr$_x$MnO$_3$ with $x = 0.3$ (LSMO-30) and $x = 0.4$ (LSMO-40) prepared by solid state reaction method, and then subjected to mechanical ball milling at different times of 3, 6 and 12 h. All of the samples were characterized by X-ray diffraction (XRD) and magnetic measurements. From Rietveld analysis of XRD patterns it was found a reduction in crystallite average size ($D_v$) with increasing milling time, for both concentrations. For LSMO-30 sample a mix of two different crystallographic structures, an orthorhombic phase (Pnma), and another rhombohedral (R$_3$C) were identified at 3 and 6 h, but for 12 h of milling the R$_3$C structure was the only phase identified. In contrast, for LSMO-40 the R$_3$C structure was discerned as the unique phase independent of milling time. For both samples, a low value of the saturation magnetization was obtained for the longer milling time (smaller $D_v$). This behaviour was attributed to surface effects that induce magnetically disordered states with decreasing of particle size. This magnetic anisotropy surface was also evidenced on Zeta potential values and the changes of coercive fields, which increased most drastically with the first hours of mechanical ball milling time.

1. Introduction

Magnetic nanomaterials have been an interesting subject of numerous investigations in recent years, because they can exhibit properties that are not observed in their bulk form. Particular attention have received the perovskite manganites $R_{1-x}A_x$MnO$_3$ (where $R$ and $A$ are rare earths and alkaline earths respectively), which present the Colossal Magneto resistance (CMR) phenomenon, in addition to properties with potential applications in different areas [1]. Particularly, La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) manganite has earned important attention as a potential candidate for technological application, due to its high transition Curie temperature (Tc), good conduction by spin-polarized, different phase structural in a variety of range of x concentration, among others; besides to present CMR effect [2]. In the last years, technological efforts have been dedicated to improve synthesis methods to preparations of LSMO.
particles, at nanometric scale, in order to control morphology, size, and chemical stability of LSMO nanoparticles (NPs) [3-5]. Currently, these efforts have a particular interest, in order to use these NPs as a magnetic core and to be coated by other layers of different materials, which can be applicable for example for biomedical purposes in drug loading and release [6]. In composites it is possible to functionalize nanomaterials through assembly of nano-LSMO with multiferroics systems [7]. The main interest is associated with the surface behavior of the NPs when they show a tendency to agglomerate, resulting in increased particle size due to the high surface area to volume ratio [8]. Thus, suitable surface functionalization of the particles and choice of solvent are important to avoid aggregation. Based on these considerations, methods as co-precipitation, electrochemical and sol-gel allow obtaining fine particles, with different homogeneity and size ranges, depending of annealing temperature. Mechanical milling process is another method for the preparation of NPs and homogenization of crystallographic phase of interest, independent of chemical composition. Depending on the synthesis method used, it is important to understand how the physical properties of the system are related with structural, morphological and surface changes after its obtaining. Taking into account this information and also the fact that the LSMO have magnetic properties interesting; the main aims of this study is to evaluate the influence of the reduction of particle size, with the different properties (structural, magnetic, and surface) of La$_{1-x}$Sr$_x$MnO$_3$ powders (with $x=0.3$ for LSMO-30 and $x=0.4$ for LSMO-40) fabricated by solid state reaction method. LSMO-30 and LSMO-40 samples were subjected to mechanical grinding processes for several hours (3, 6 and 12 hours) under atmospheric conditions.

2. Experimental part

Pure phases of ferromagnetic manganites La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO-30) and La$_{0.6}$Sr$_{0.4}$MnO$_3$ (LSMO-40) were prepared by the standard solid state reaction. First, the powders were pre-calcined at 900°C for 12 h. Next, the samples were annealed at 1200°C for 24 h and finally were calcined at 1300°C for 6 h. All of the processes of sintered were carried out in air atmosphere. In order to reduce particle size, LSMO powders were divided into four parts and subjected to mechanical milling in a planetary ball mill Frithsh Pulverisette 5. The milling was carried out at air atmospheric conditions by using of jars and stainless-steel balls. The ball-to-powder ratio used was 20:1 and a rotational speed of 250 rpm (collision energy). In this study different milling time of 0, 3, 6 and 12 h was evaluated. Each sample was milled for intervals of 1 h and break periods of 30 min up to completion of the desired milling time. X-ray diffraction (XRD) patterns were collected using a Panalytical, Empyream Serie 2 diffractometer with a Cu Kα source ($\lambda = 1.5406$ Å) in Bragg-Brentano geometry. The data were collected in the range of 2θ = 20–80 in 2θ with a step size of 0.013° and step time of 3 s. The XRD patterns were fitted using the Rietveld method to obtain crystal lattice parameters and average crystallite size. To investigate the milling time effect on the powders, a distribution grain size was measured by using Dynamic Light Scattering (DLS). Magnetic measurements were performed via vibrating-sample magnetometer technique (VSM) with the physical properties measurement system (PPMS) Quantum Design. Magnetization hysteresis loops $M(H)$, were measured in the ranges of applied field from -5 kOe to 5 kOe, with an step of 0.015 kOe, and a resolution of $\sim 10^{-6}$ emu, of magnetic moment.

3. Results and Discussion

Previous works for the same authors, reported the x-ray measurements and the Rietvel refinement, for the two concentrations of the LSMO manganite studied here, at different milling times. Table 1 collected the original results obtained [9, 10]. From Table 1, it can be seen that in the LSMO-30 samples, the lattice volume ($V$) of the rhombohedral, R3C, crystal system decreases, while for the orthorhombic, Pnma, phase increases monotonically as milling time increases. According to Rietveld method a mix of rhombohedral and orthorhombic phases were identified in this sample. With increasing milling time (3
and 6 h) a gradual decrease of the Pnma phase was observed, and when a 12 h of milling is reached, a single R3C phase becomes stabilized. On the other hand, for LSMO-40 the lattice volume (V) values, remain almost constant in the whole range of milling, indicating the unique presence of R3C crystal structure. For both sets of manganites the crystallite average sizes \(D_v\) decreases with increasing the milling time, obtaining an average around 21 nm at the highest milling time (12 h).

**Table 1.** Structural parameters extracted from Rietveld analysis for LSMO-30 and LSMO-40 samples at different milling times. The crystallite average sizes \(D_v\) are also presented.

| Sample | \(a = b\) (Å) | \(c\) (Å) | \(V\) (Å³) | \(D_v\) (nm) | wt (%) | \(R_F\) (%) | \(\chi^2\) |
|--------|----------------|--------|---------|---------|-------|---------|---------|
| **LSMO-30** | | | | | | | |
| NM     | 5.5021 (4)     | 13.3607 (5) | 350.28 (8) | 82.7 (4) | 84   |        |        |
| 3 h    | 5.4986 (9)     | 13.3509 (4) | 349.58 (5) | 36.8 (3) | 90   |        |        |
| 6 h    | 5.4962 (6)     | 13.3502 (6) | 349.26 (5) | 26.5 (2) | 94   |        |        |
| 12 h   | 5.4959 (3)     | 13.3450 (7) | 349.08 (6) | 20.9 (2) | 100  |        |        |
| **LSMO-40** | | | | | | | |
| NM     | 5.4768 (2)     | 7.7377 (2)  | 5.196 (3)  | 233.91 (5) | 70.5 (4) | 16    | 2.60   | 1.31 |
| 3 h    | 5.4951 (3)     | 7.7088 (6)  | 5.5249 (5) | 234.04 (5) | 32.5 (3) | 10    | 2.24   | 1.14 |
| 6 h    | 5.5251 (2)     | 7.7512 (4)  | 5.5279 (4) | 236.74 (7) | 24.4 (2) | 6     | 2.38   | 1.21 |
| 12 h   | ---            | ---         | ---       | ---       | ---    | ---   | 2.51   | 1.32 |

Mechanical milling process is a sensitive factor for homogenization of a crystallographic phase. The results obtained in this work suggest that the stoichiometric composition of the manganate is highly sensitive to the amount of La and Sr incorporated into of material and can be considered as a crucial parameter in the stabilization of the R3C phase. In particular, depending on the stoichiometric composition, for the manganate doped with Strontium an R3C structure is expected to be the most stable [11]. Particularly, \(La_{0.67}Sr_{0.33}MnO_3\) is the concentration limit where a change in the structural phase occurs, from orthorhombic to rhombohedral. Mechanical milling process can play an important role in the transformation to a single and more stable phase, when a mix of two different manganites structures are obtained, as is the case of LSMO-30.

Figure 1 displays the particle volume distribution. It can be seen that the grain size lies in the range of 50 nm to 100 µm for both LSMO-30 Fig 1(a), and LSMO-40 Fig 1(b) samples. Although milling times defined in this work are rather small, a wide variation in grain size (and crystallite) with milling time is observed. This is due to competing between particle fragmentation and the agglomeration process [12]. Additionally in Table 2, the results of the mean particle sizes \(d_{50}\) are presented. From the \(d_{50}\) values, it can be suggested that after 6 hours of milling the grain size remain almost constant for LSMO samples and increment of milling times is unnecessary. Results show that the initial material has the higher grain size and this particle size decrease significantly after 3h of milling. In this first milling, the grain size decreased approximately to 1/5 part of the original size for both samples. When the samples were milled during 6h the grain size increases slightly, stabilizing at a value near to 4.3 µm and 4.5 µm for LSMO-30 and LSMO-40 respectively. For milling times higher that 6h the grain size remain almost constant.
Gaussian analysis for each of the peaks of the distribution was done. It is found that both samples, before milling, have two particle types that correspond to observed maxima. LSMO-30 has maxima in 10 and 65 μm with a standard deviation of 15 and 35 μm respectively. LSMO-40, has the maximum in 6 and 29 μm with a standard deviation of 16 μm in both peaks. In both samples it is observed that the average size of the particles decreases with the milling time, and in the same way the standard deviation decreases. For 12 h of milling, in LSMO 30, the maxima are around 3 and 18 μm with a standard deviation of 16 μm; and for LSMO-40, the maximum of 3 and 15 μm have a standard deviation of 10 μm.

**Table 2.** Average grain size for LSMO-30 and LSMO-40

| Milling time (h) | LSMO-30 d50 (±0.1μm) | LSMO-40 d50 (±0.1μm) |
|-----------------|----------------------|----------------------|
| NM              | 10.0                 | 15.1                 |
| 3               | 2.6                  | 3.8                  |
| 6               | 4.2                  | 4.6                  |
| 12              | 4.3                  | 4.5                  |

Zeta potential measurements were also performed (See Table 3), in LSMO-30 and LSMO-40 samples. In general, zeta potential measurements specifies the electro kinetic potential of a colloidal system. This is a physical property which is exhibited by any particle in a suspension. Magnitude of the zeta potential gives the net charge at the diffuse boundary of a particle in a suspension which will ultimately indicate the potential stability of a colloidal system. If particles have small zeta potential values, there is no force to prevent particle coming together and their aggregation. It is generally considered that the zeta potential values greater than +30 mV or smaller than -30 mV, result in stable suspensions. However these values can slightly change depending on several factors such as density and pH. For LSMO samples, the Zeta potentials were performed at neutral pH. Despite that some variations in the Zeta potential value, on the first 6 hours of milling, are observed, the suspensions are no stable.
Table 3. Zeta potential measurements for LSMO-30 and LSMO-40

| Milling time (h) | LSMO-30          | LSMO-40          |
|------------------|------------------|------------------|
|                  | Zeta potential  | Zeta potential  |
|                  | (± 5mV)         | (± 5mV)         |
| NM               | -19.5           | -18             |
| 3                | -9.34           | -2.96           |
| 6                | 8.4             | 0.38            |
| 12               | -0.99           | -10.7           |

Respect to magnetic properties, the magnetic moment of LSMO manganite depend of the particle size. In general, over all range of temperature, samples without milling present higher magnetic moment value than that corresponding to 12 hours of milling. Saturation magnetization $M_s$, calculated at 300K from hysteresis loops from 0 to 5 kOe, showed dependence with grain size. Samples without milling process showed a high $M_s$, around 50 emu/g and 25 emu/g for LSMO-30 and LSMO-40 respectively. Time of 12h of milling produced smaller saturation magnetization. Fig. 2 (a), collected the $M_s$ values, calculated for all samples, as a function of milling time. This behaviour can be attributed to surface effects, since a decreasing in the grain size produces changes in the crystallographic structure and this leads to magnetic disorder. This disorder manifests with a decrease in the ferromagnetic state, which increases with diminution of particle size [12].

This is in accordance with the coercive field, $H_c$, measured at room temperature; see Fig. 2 (b). A magnetic anisotropy surface is evidenced when the coercivity increases. However, the coercivity suffer drastic changes only to 3h of milling time, in both samples. After that, $H_c$ keeps around 20 Oe, similar for 6 and 12 h of milling. Milling process can induce the surface disorder, increasing the magnetic energy at low temperature.

The results show that both the particle size and the Zeta potential, along with the coercivity, change drastically in the first hours of mechanical milling, for both LSMO concentrations. Probably, the most important structural and magnetic disorder, is manifested in the first hours of milling process.

4. Conclusions

In summary, the properties of manganite La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO-30) and La$_{0.6}$Sr$_{0.4}$MnO$_3$ (LSMO-40) powders, subjected to different milling time by mechanical ball milling, have been studied. The results show the relation between structural and magnetic properties with decreasing of grain size. Particularly, mechanical grinding, can favor the stabilization and homogenization of a single crystalline phase (corroborated by Rietveld analysis), depending of the stoichiometric structure. Samples studied in this
work, showed dependence with the surface effects for higher milling time, which was evidenced by decreasing saturation magnetization with the particle size, and increased coercive fields. Zeta potential values and the coercivity change drastically in the first hours of mechanical milling, for both LSMO samples. Probably, the most important structural and magnetic disorder, which decrease the ferromagnetic state in the particles, is manifested in the first hours of milling process. This results, can help to understand the physical properties of LSMO particles during milling processes.

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References
[1] M. B. Salamon, M. Jaime, Rev. Mod. Phys. Vol 73 (2001) 583; M. Kacenka, et al; J. Colloid Interface Sci. 447 (2015) 97; C. P. Reshmi, et al; Solid State Sci. 19 (2013) 130.
[2] L.E. Hueso, J.M. Pruneda, V. Ferrari, G. Burnell, J.P. Valdés-Herrera, B.D. Simons, P.B. Littlewood, E. Artacho, A. Fert, N.D. Mathur, Nature 445 (2007) 410.
[3] H. Baaziz, A. Tozri, E. Dhahri, E.K. Hlil, Solid State Commun. 208 (2015) 45.
[4] R. D. Sánchez, J. Rivas, C. Vásquez-Vásquez, A. López-Quintela, M. T. Causa, M. Tovar and S. Oseroff, Appl. Phys. Lett. Vol 68 (1996) 134-136.
[5] Kumar Navin, Rajnish Kurchania, Ceramics International, Volume 44 (2018) 4973-4980.
[6] Sonali Biswas, et al; Phase Transitions, (2016); 1-10, DOI: 10.1080/01411594.2016.1156681
[7] Shreeja Pillai, et al; J. Appl. Phys. 122 104101 (2017); doi: 10.1063/1.5001566.
[8] Tiffany Marin, et al; J. Phys. Chem. B 120 (2016) 6634-6645.
[9] G. Campillo, A. Gil, O. Arnache, J. Osorio, G. Sierra, Journal of physics:conference series 466 (2013) 012022
[10] Gloria Campillo, et al; Revista EIA (Mayo 2014) E31-E38.
[11] G. Venkataiah, V. Prasad, P. Venugopal Reddy, J. Alloys and Compounds. Vol 429 (2007) 1-9.
[12] P. Kameli, H. Salamati, A. Aezami, J. Alloys and Compounds. Vol 450 (2008) 7-11.