Structural and magnetic properties of nanoparticles of La$_{2/3}$Sr$_{1/3}$MnO$_3$

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Abstract

Nanoparticles of the La$_{2/3}$Sr$_{1/3}$MnO$_3$ manganite were synthesized using the Pechini process and their structural properties were characterized by X-ray diffraction (XRD) and by transmission electron microscopy (TEM). The magnetization of compacted powders was measured for temperatures in the range 190 $\leq T \leq$ 450 K. The estimated average diameter ($D$) of the particles continuously increased from 20 to 95 nm when the calcination temperature was varied from 873 to 1273 K. From the magnetic data we found that the room temperature saturation magnetization scaled with $1/D$ while the magnetic transition temperature follows a $D^2$ power-law suggesting that the correlation length $\xi$ is mainly determined by the surface properties of the nanoparticles.

Keywords: Manganites; Nanoparticles; Magnetism

1. Introduction

Doped manganites in the form La$_{1-x}$A$_x$MnO$_3$ (where A is a divalent cation) has attracted considerable scientific and technological interest lately due to some peculiarities exhibited in their transport properties [1]. The structural and magnetic properties are interdependent and the manganites present very large variations in the magnetoresistance, namely, colossal magnetoresistance (CMR). Even though the transport properties are an intrinsic phenomenon in manganite with mixed valence, extrinsic factors such as the size of the grain and the grain boundaries influence enormously the CMR [2,3], especially if the grains are in the nanometric scale.

It is known that ferromagnetic particles with diameter smaller than a critical size ($D_c$) become single domain. For manganites this critical diameter is around 80 nm as determined by Sánchez et al. [4]. Furthermore, the number of atoms at the surfaces of nanoparticles is comparable to that in their bulks. Thus, surface effects become important in this particle size regime, influencing, for instance, the correlation length $\xi$. It is also known that some manganites have their magnetic transition temperature $T^*$ increased when the particle size are also increased [3,5]. In this work, we show that $T^*$ measured for nanoparticles of the manganite La$_{2/3}$Sr$_{1/3}$MnO$_3$ with size varying from 20 to 95 nm follows a scaling law with $\xi$ which, in turn, is proportional to $D^2$. As far as we know, this is the first time that this kind of scaling is used to correlate the magnetic properties with the surface area of the particles.

2. Sample preparation and techniques

Powders with nanoparticles of La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO) were prepared using the Pechini method. In this process, stoichiometric amounts of the precursor reagents La(NO$_3$)$_3$·6H$_2$O, Mn(NO$_3$)$_2$·4H$_2$O and Sr(NO$_3$)$_2$ were dissolved in water and mixed with ethylene glycol (EG) and citric acid (CA), forming a stable solution. This solution was then heated on a thermal plate under constant stirring at 333 K to eliminate the excess of water and to accelerate the esterification reaction. As the polymerization reaction proceeds, a homogeneous sol solution is obtained and further heating to remove the excess of solvent leads to an intermediated resin. The resin was then

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calcinated at 673 K for 1 h in air before final sintering for 1 h at temperatures varying in steps of 100 K from 873 to 1273 K. The structure and morphology of the powder were analyzed using X-ray diffraction (XRD) using a Cu-Kα radiation source, and transmission electron microscopy (TEM), respectively. The mean sizes of the diameters of the particle were determined using the Rietveld refinement procedure. The X-ray diffraction data showed that the material annealed above 873 K produced single phase and highly crystalline particles. The magnetization of the particle as a function of the temperature was measured using a vibrating sample magnetometer while the low-frequency (1 kHz) magnetic susceptibility was measured using a first-order gradiometer AC susceptor.

3. Experimental results

All the X-ray patterns obtained for the samples produced as described above were indexed assuming an orthorhombic perovskite crystalline structure belonging to the space group Pbnm. The increase in the sintering temperature resulted in an increase in the volume of the unit cell ($\Delta V/V \approx 0.46\%$), as well. The Rietveld refinement of the X-ray data yielded the mean sizes of the diameter of the crystallites. They were 20.2, 24.4, 32.4, 49.0, and 95.4 nm, for samples synthesized at 873, 973, 1073, 1173 and 1273 K, respectively.

Fig. 1 shows the transmission electron microscopy (TEM) images for the powders calcinated at 873 K (A) and 1173 K (B). The size of the particles observed in the TEM images are comparable to those obtained from the Rietveld refinement. Thus, in our analysis we considered the average size of the crystallites equal to the average size of the particles. The room temperature magnetization measured as function of the applied magnetic field is shown in Fig. 2. From the $M$ vs. $H$ data one can find that the saturation magnetization varies with inverse of the mean particle size. This result is shown in the inset of Fig. 2 were $M_S$ is plotted against $1/D$. This linear dependence with $1/D$, the surface to volume ratio, is a clear indication that the degree of crystallization is the same for all the samples studied. Besides, the fact that the reduction in the magnetization is only a function of the particle size indicates that the magnetic dead layer is approximately the same for all the samples [6]. The upper right insert in Fig. 3 shows the magnetization versus temperature curves measured in an applied magnetic field of 50 Oe, normalized by the value measured at 190 K, for five powder samples compacted in a non-magnetic sample holder. From these curves, one can see that the magnetic transition temperature $T^*$, increases from 304 to 360 K for the sample annealed at 873 and 1273 K, respectively. $T^*$ is better defined by the peak in the first derivative of the AC susceptibility as shown in the lower right insert in Fig. 3 [7]. Variations in $T^*$ with the annealing temperature were also observed in LMSO manganites but the measurements were made in samples prepared by sol–gel and pyrolysis method [3,5].
particle systems yielded a similar dependence for $T^*$ with particle size, governed by this finite-scaling law \[9\].

4. Discussions and conclusions

The manganite nanoparticles used in this work had their mean size within the 20–95 nm range. In this size regime most of particles are single magnetic domain and surface effects influence the magnetic properties of the particles with size close to $D_C$ (80 nm). Furthermore, the magnetic transition temperature $T^*$ can be described in terms of the correlation length $\xi$ through the following scaling law \[8\] $(T^* - T^\infty)/T^\infty = (\xi/\xi_0)^{-1/\nu}$, where $T^\infty$ is the transition temperature for a bulk sample ($\xi \to \infty$), $\xi_0$ is the characteristic correlation length and $\nu$ is a critical exponent. In the blocked single domain particle regime $\xi$ is proportional the area of the surface of the particles. Thus, the scaling law, using $\xi/\xi_0 = (D/D_0)^2$, can be written as $T^* = T^\infty[1 - (D/D_0)^{-2/\nu}]$, where $D_0$ is a characteristic dimension of the system. We were able to make a good fitting of this expression to our $T^*$ vs. $D$ data using as the fitting parameters $T^\infty = 363.3$ K, $D_0 = 7.4$ nm and $\nu = 1.0$. Indeed, this remarkable curve fitting, covering almost two decades in particle size, is actually done with two adjusting parameters only, $D_0$ and $\nu$, since $T^\infty$ can be measured independently. The values yielded by the fitting are in very good agreement with those reported in the literature \[10\] for other manganite system.

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References