



# Magnetic anisotropy and superparamagnetism in $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ , $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ and their mixed composition $0.875 \text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3/0.125 \text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ , agglomerated at different temperatures

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## H I G H L I G H T S

- Presence of PM-SPM transition at the irreversibility temperature.
- Existence of superparamagnetism (SPM) clusters within the FM phase.
- The origin of this superparamagnetism phenomenon is the nanometric size.
- Saturation magnetization was observed to increase with increase in particle size.
- Evidence of formation of a magnetically ferrimagnetic layer at the surface.

## A R T I C L E I N F O

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## A B S T R A C T

The static magnetic properties of nano-particles  $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$  (SOC1),  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  (S1C0) and the  $0.875(\text{SOC}1)0.125(\text{S}1\text{C}0)$  composition sintered at different temperatures, SC. 4-1 (700 °C), SC. 4-2 (900 °C), SC. 4-3 (1100 °C) and SC. 4-4 (1300 °C), have been investigated by the *dc* magnetic susceptibility, FC and ZFC magnetization, isothermal magnetization  $M(\mu_0H, 5 \text{ K})$  measurements and hysteresis loop at different temperatures. The nano-metric size of the studied compounds, determined by using the Scherrer formula and partially supported by TEM images, is at the origin of superparamagnetism phenomenon encountered in the compounds studied below the Curie temperature. The evolution of the Curie temperature is explained by the cationic disorder in A-site. To explain the difference between the theoretical and experimental values of the magnetization saturation, it has been adopted the Core-shell model.

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## 1. Introduction

Over the past decades, perovskite manganites of the type  $(\text{R}_{1-x}\text{M}_x)\text{MnO}_3$  (where R is a trivalent rare earth ion and M is a divalent alkali earth ion) have attracted attention due to their interesting physical properties such as colossal magnetoresistance (CMR), magnetocaloric effect (MCE), charge ordering, orbital ordering and spin ordering [1–11]. In particular, the doped manganites  $\text{La}_{1-x}\text{M}_x\text{MnO}_3$  (M = Ca, Sr, Ba) show a variety of physical properties

resulting in a rich phase diagram depending on the dopant and its concentration. Among the various manganites compounds,  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  and  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  systems have received a lot of attention because, over the entire composition range, these systems exhibit rich magnetic and electrical phase diagram [12–15]. Particularly,  $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$  and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  compositions belong to one of the two most intensively studied series of manganites [16–21], due to the strong coupling between magnetic structure and crystal lattice distortions. These two compounds, having a similar ratio of  $\text{Mn}^{3+}/\text{Mn}^{4+}$  but different average ionic radius of the A-cation site, present a ferromagnetic (FM) order below the critical temperature  $T_C$  ( $\approx 260 \text{ K}$  for  $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$  and  $\approx 370 \text{ K}$  for  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ ). On the other hand, if the size of the

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system is comparable to one of the length scales of the magnetic coupling at work in that system, the behavior can be quite different from that of the bulk sample. Magnetic nano-particles have attracted a great deal of interest in recent years thanks to their applications in nano-technology, such as magnetic recording media, magnetic sensors, permanent magnets and ferrofluids as well as in biomedicine [22–26]. For nano-particles, supposed spherical, with diameters lower than the critical diameter [27],

$$D_c = \frac{72\sqrt{A \cdot K}}{\mu_0 M_s^2} \quad (1)$$

where  $A \approx 10^{-11} \text{Jm}^{-1}$  is the exchange stiffness parameter,  $K$  the uniaxial anisotropy constant,  $\mu_0$  the vacuum permeability and  $M_s$  the saturation magnetization, the single domain state is energetically stable. In sufficiently small nano-particles, magnetization can randomly flip direction under the influence of temperature. When the size of a particle is very small, the thermal energy  $k_B T$  may be enough to overcome the anisotropy barrier, resulting in the occasional magnetization spontaneous rotation. The typical time between two flips is called the Neel relaxation time. With no external field, this yields an average magnetization of zero, with the averaging done either over time or over multiple particles. In the absence of an external magnetic field, when the time used to measure the magnetization of the nano-particles is much longer than the Neel relaxation time, their magnetization appears to be in average zero. They are said to be in the superparamagnetic (SPM) state. When an external field is present, the particle has an average magnetization parallel to the field. In this state, an external magnetic field is able to magnetize the nano-particles similarly to a paramagnet. However, their magnetic susceptibility is much larger than that of paramagnets. The approach of thermally activated switching of a single-domain particle is called the Neel-Brown model. The average time  $\tau_N$ , called the Neel relaxation time, taken for the thermal energy to flip the magnetization can be expressed using the Arrhenius-Neel law [28]:

$$\tau_N = \tau_0 \exp\left(\frac{KV}{k_B T}\right) \quad (2)$$

with  $\tau_0$  the resonance relaxation time of the spin system, which is generally around the order of  $10^{-9} \text{s}$  [29].  $K$  is the magnetic anisotropy of the grain and  $V$  its volume,  $k_B$  is the Boltzmann constant and  $T$  is the temperature.

The diameter  $D_{th}$  below which the SPM limit occurs is:

$$D_{th} = \sqrt[3]{\frac{6k_B T}{\pi K} \ln\left(\frac{\tau_N}{\tau_0}\right)} \quad (3)$$

The SPM limit is a real issue for the current generation of hard disks, since magnetic bits cannot grow smaller than that without losing data.

The aim of this work is to study the effect of the particle size and magnetic anisotropy on the magnetic behaviors of  $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ / $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  mixtures prepared via citric-gel method, which generally leads to the formation of nano-particles.

## 2. Experiment

The polycrystalline samples of  $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$  (SOC1) and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  (S1C0) were prepared via citric-gel method. The (0.875(SOC1)/0.125(S1C0)) composition was obtained by a stoichiometric proportion of the (SOC1) and (S1C0) powders. By sintering the composition, at various temperatures of 700 (SC.4-1), 900 (SC.4-2), 1100 (SC.4-3) and 1300 °C (SC.4-4) in air, four samples

were prepared. The method of preparation, the effect of the annealing temperature on the structural and magnetic properties  $M(T)$  were discussed in our previous work [30].

The position and full width at half maximum of the most intense peak, crystallite size, and micro-strain are determined from Fullprof refinement to XRD powder diffraction data.

The morphologies of the surfaces and fracture surfaces of all samples were observed by Transmission Electron Microscopy (TEM). This technique was employed to obtain the bright field (BF) images of the samples, and thus, to prepare a histogram of particle size and analyze its morphology.

The magnetization curves  $M(T)$ , in the zero-field cooling (ZFC) and field cooling (FC) modes, were obtained under an applied magnetic field of 0.05 T with a temperature ranging from 5 to 500 K. In the FC mode, the sample was cooled from a temperature above the critical temperature to 5 K under the magnetic field of 0.05 T. The magnetization is measured as the temperature being cooled. For ZFC measurements, the sample was cooled from room temperature to 5 K in zero magnetic field and at 5 K a magnetic field of 0.05 T was applied then measuring the magnetization ( $M$ ) as the sample heated to desired temperature.

The isothermal magnetization curves  $M(\mu_0 H)$  of samples was measured at temperature 5 K under an applied magnetic field varying from 0 to 10 T.

The hysteresis cycles, at temperatures slightly below the Curie temperature and at magnetic fields between  $-10$  T and  $10$  T, were performed.

## 3. Results and discussion

As mentioned in our previous work, the two parent compounds SOC1 and S1C0 were found to crystallize in the rhombohedral structure with  $R\bar{3}c$  space group and orthorhombic system with the  $Pbnm$  space group, respectively [30]. The compounds sintered at 700 (SC. 4-1) and 900 °C (SC. 4-2) were found to present the two rhombohedral and orthorhombic phases corresponding to the parent compounds, which indicates that no interfacial reaction occurs. Finally, it is concluded that, when augmenting the sintering temperature to 1100 (SC. 4-3) and 1300 °C (SC. 4-4), there is a formation of the new  $\text{La}_{0.6}\text{Ca}_{0.35}\text{Sr}_{0.05}\text{MnO}_3$  phase [30].

From the magnetic study, it has been noted that SOC1, S1C0 and SC.4-4 compounds exhibit paramagnetic-ferromagnetic (PM-FM) transitions. However, the SC.4-1 and SC.4-2 compounds, the composites of the two SOC1 and S1C0 parent compounds, present two magnetic transitions corresponding to the SOC1 and S1C0, which confirms the structural observations. In fact, by comparing the magnetization  $M(T)$  of (SC.4-1) and (SC.4-2) compounds and that of  $0.865 \times M(\text{SOC1}) + 0.135 \times M(\text{S1C0})$  composite (Fig. 1) these magnetizations were found to be substantially equal.

$$M(\text{SC 4 - 1, 2}) = 0.865 \times M(\text{SOC1}) + 0.135 \times M(\text{S1C0}) \quad (4)$$

This result confirms that the two SC. 4-1 and SC. 4-2 compounds are composites from SOC1 and S1C0 with (0.865/0.135) mass fractions.

### 3.1. Correlation between disorder and magnetic properties

The insets in Fig. 2 show the strong correlation between cationic disorder in A-site and magnetic properties. With increasing Sr-content, the unit cell volume increases monotonously from 56.947 for  $x = 0$  to 58.012 Å<sup>3</sup> for  $x = 0.4$  (Fig. 2-a). This behavior can be explained in terms of average ionic radius values of the A-site. In fact, the ionic radius of strontium is higher than that of calcium. The same change is observed for the Curie temperature (Fig. 2-b) and

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