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Critical properties in $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ manganite: A comparison between sol-gel and solid state process

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ABSTRACT

The critical properties of $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ manganite elaborated using two different methods have been investigated around the ferromagnetic-paramagnetic phase transition. Our sample was successfully synthesized by solid-state reaction (S1) and sol-gel route (S2). The X-ray diffraction characterizations show that (S1) crystallized in orthorhombic structure with *Pnma* space group without any detectable impurity. Though, (S2) crystallized in rhombohedra structure with *R-3C* space group. Various techniques such as modified Arrott plots, Kouvel-Fisher method and critical isotherm analysis were used to determine the values of the Curie temperature T_C, as well as the critical exponents β (corresponding to the spontaneous magnetization), γ (corresponding to the initial susceptibility) and δ (corresponding to the critical magnetization isotherm). The estimated results are close to those expected by the mean-field model for sample S2; while for sample S1, the exponents values are close to those expected using the tricritical model. The obtained values from critical isotherm M (T_C, $\mu_0 H$) are close to those determined using the Widom scaling relation, and also there are found to follow scaling equation with the magnetization data scaled into two different curves below and above T_C, which implies the reliability and accuracy of the exponents. The change of the universality class can be explained by the reduction of the grain size. These results show that the critical behavior of our sample depend havely on the synthesis technique.

1. Introduction

Perovskite type manganites $Ln_{1-x}A_xMnO_3$ (Ln is a trivalent rare-earth and A is a divalent alkaline-earth) have attracted great attention because of their wonderful magnetic and electronic properties as well as their technological potential applications [1–7]. These materials exhibit a rich variety of physical properties. The most accepted interpretations for the cause of these properties are the double exchange model [8] and Jahn–Teller effect [9,10]. On one hand, these properties can be controlled by doping with suitable elements in the A-site and/or B-site to change the structural parameters and/or the Mn^{3+}/Mn^{4+} ratio. On the other hand, these properties depend strongly on the experimental conditions. Moreover, several studies in literature which emphasizes on the rare-earth manganite perovskites found that some of the basic physical properties depend strongly on the synthesis method, such as the effective morphology, the chemical composition, the grain size distribution and their correlation with magnetic and magnetocaloric properties [11–13]. Such studies deeply affect the physical and chemical properties of the materials prepared by the various elaborating routes and they never resort to the study of this effect on critical properties. For this reason, it is necessary to investigate in details the correlation between the synthesis conditions and critical exponents around the paramagnetic-ferromagnetic transition. The critical behavior analysis for these materials can provide important information about the thermodynamic observations above and below T_C; especially that recent theoretical calculations have predicted that the critical exponents in manganites could not be included in a universality class [14–17]. Four different theoretical models such as mean field ($\beta = 0.5$, $\gamma = 1.0$ and $\delta = 3.0$), three-dimensional (3D) Heisenberg ($\beta = 0.365$, $\gamma = 1.336$ and $\delta = 4.8$), three-dimensional (3D) Ising ($\beta = 0.325$, $\gamma = 1.24$ and $\delta = 4.82$) and tricritical mean field ($\beta = 0.25$, $\gamma = 1.0$ and $\delta = 5.0$) were used to discuss the critical properties in manganites. Consequently, it is substantial to understand how elaborating methods affect various

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aspects of the physical properties of manganites. One of the most studied compounds in the last few years is the $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ system. Depending on the variation of both dopant concentration and sintering temperature, this system undergoes a structural transition between the orthorhombic and the rhombohedral structure at a threshold concentration of $x = 0.1$. From this reason, an essay has been made to comprehend the effect of elaborating method on the critical properties in $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ manganite prepared differently, characterized in the fact with a T_C around room temperature together with a first order-second order magnetic transition [18], where the critical exponents β, γ, and δ have been estimated reliably using different analytical methods such as the modified arrott-plot, the Kouvel-Fisher method and the critical isotherm analysis. In addition, we demonstrate that the process of elaboration presents an intensive impact on the critical properties.

2. Experimental details

$La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ powder sample was synthesized using both solid state route and sol-gel reaction (denoted S1 and S2 respectively). Starting with La_2O_3, $CaCO_3$, $SrCO_3$ and MnO_2 precursors with high purity (up to 99.9%) according to the reaction:

$$0.35\ La_2O_3 + 0.2\ CaCO_3 + 0.1\ SrCO_3 + MnO_2 \rightarrow La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3 + \delta O_2 + \delta' CO_2$$

2.1. Solid-state reaction: (S1)

The starting precursors were mixed in stoichiometric proportions in an agate mortar and the obtained mixture was calcinated at 900 °C in air for 24 h. It was then pressed into pellets of 12 mm diameter and 1 mm thickness under an axial pressure of 4 tons for 2 min and sintering at 1200 °C for 48 h after regrinding and repelling processes to ensure a better crystallization.

2.2. Sol-gel route: (S2)

The stoichiometric amounts of precursors were dissolved in dilute nitric acid at 70 °C and then a suitable amount of citric acid and ethylene glycol as coordinate agents were added. The resulting gel was decomposed at 300 °C to insure the propagation of a combustion which transforms the gel into a fine powder. Then, the sample was calcined at 600 °C. The obtained powder was then pressed into pellets (of about 1 mm thickness under an axial pressure of 4 tons for 2 min) and sintered at 1200 °C for 24 h to improve crystallinity.

The structure and phase purity were checked by powder X-ray diffraction (XRD) using CuK_α radiation ($\lambda = 1.54059$ Å) at room temperature. The pattern was recorded in the $10° \leq 2\theta \leq 70°$ angular range with a step of 0.02°. The morphology of the samples was observed with a scanning electron microscope (SEM). The magnetic measurements were carried out using a vibrating sample magnetometer (VSM). In order to accurately extract the critical exponents of our sample, magnetization isotherms were measured in the range of 0–5 T with a temperature interval of 2 K in the vicinity of the Curie temperature (T_C).

3. Scaling analysis

It is noted that the values of critical exponents β, γ and δ of $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ manganite sample are obtained, from magnetization measurements through below asymptotic relations [19]. For this intention, careful measurements were made of the magnetization at several magnetic fields at various temperatures in the critical region, both below and above Curie temperature. From the temperature dependence of M_S we have found the critical exponentβ, given by:

$$M_S(T) = M_0(-\varepsilon)^{\beta} \quad (1)$$

where M_0 is critical amplitudes, and $\varepsilon=(T - T_C)/T_C$ is the reduced temperature.

Also, the critical exponent γ has been established from the temperature dependence of the inverse of susceptibility χ_0^{-1}, which is given by

$$\chi_0^{-1}(T) = \left(\frac{h_0}{M_0}\right)\varepsilon^{\gamma} \quad (2)$$

where h_0 is the corresponding critical amplitude.

Again, from the magnetic applied field, the dependence of magnetization M at T_C given by:

$$M = D(H)^{1/\delta} \quad (3)$$

we have found δ, where D is the critical amplitude.

We have also shown that the exponents β, γ and δ follow the static scaling relationship:

$$\delta = 1 + \gamma/\beta \quad (4)$$

The magnetic equation of state is a relationship among the variables M ($\mu_0 H$,ε), $\mu_0 H$ and T. Using scaling hypothesis this can be expressed as:

$$M(\mu_0 H, \varepsilon) = \varepsilon^{\beta} f_{\pm}\left(H \Big/ \varepsilon^{\beta+\gamma}\right) \quad (5)$$

where f_+ for $T > T_C$ and f_- for $T < T_C$, respectively are regular functions.

This last Eq. (5) implies that for true scaling relations and right choice of β, γ and δ values, the scaled $M/|\varepsilon|^{\beta}$ plotted as a function of the scaled $\mu_0 H/|\varepsilon|^{\beta+\gamma}$ will fall on two universal curves, one above T_C and the other below T_C. This is an important criterion of critical regime.

4. Results and discussions

The phase identification and the structural analysis of $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ manganite sample was carried out using the X-ray diffraction patterns recorded at room temperature. A typical X-Ray diffraction pattern of both samples is shown in Fig. 1. The two samples are single phase without any detectable impurity. We have refined the structure by the Rietveld method [20] using the Fullprof program [21]. The refinement shows that (S1) crystallized in orthorhombic structure with *Pnma* space group and (S2) crystallized in rhombohedra structure with R-3C space group. These results are in agreement with those elaborated by the hydrothermal synthesis process [22] and the single crystal elaborated by floating-zone [23].

The measured manganite density (D) is found to be 6.20 and 6.19 (g/cm^3) for (S1) and (S2) respectively. The XRD density (D_{XRD}) was also calculated according to the following formula [24]:

$$D_{XRD} = ZM/AV \quad (6)$$

- Where: Z: the number of manganite molecules per unit cell;
- M: molecular mass;