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Critical behavior near the paramagnetic-ferromagnetic phase transition in polycrystalline $La_{0.6}Ca_{0.2}Ba_{0.15}\square_{0.05}MnO_3$

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ABSTRACT

In this paper, we present a detailed study on the structural and critical behavior around paramagnetic (PM)-ferromagnetic (FM) phase transition in $La_{0.6}Ca_{0.2}Ba_{0.15}\square_{0.05}MnO_3$ (LCBMO). Our powder specimen was synthesized using the conventional solid-state reaction method and was analyzed by X-ray diffraction and magnetic measurements. X-ray diffraction analysis, at room temperature, shows that LCBMO adopts an orthorhombic structure with Pbnm space group. Detailed analyses of magnetic-field dependences of magnetization in the vicinity of the paramagnetic-ferromagnetic transition, M(H,T), reveal that LCBMO undergoes a second-order magnetic phase transition. Critical behavior has been studied through various techniques such as modified Arrott plot (MAP), Kouvel-Fisher method (KF) and critical isotherm (CI) analysis. The estimated Critical exponents are close to those expected for the mean-field model ($\beta=0.5$, $\gamma=1$ and $\delta=3$). The reliability of the critical exponent values was confirmed by the Widom scaling relation, as well as the universal scaling hypothesis.

1. Introduction

In the recent years, increasing interest has been devoted to the large magneto-caloric effect in perovskite manganites, derived from $AMnO_3$ ($A=La^{3+}$, Pr^{3+} Nd^{3+}, Dy^{3+}, Sr^{2+}, Ba^{2+}, Ca^{2+}…) [1–4], owing to their many advantages on gas refrigeration. These compounds are characterized by large magneto-caloric effect (MCE), which favors their use in the magnetic refrigeration technology. The latter appears like an ecological alternative to the classic refrigeration based on the compression and expansion of fluids, which harms the ozone layer and threatens human existence on earth. The study of the MCE of these manganites is important, not only from the potential applications perspective, but also since it provides a tool to understand the intrinsic properties of these materials. These properties were widely interpreted by means of the double-exchange (DE) mechanism, proposed by Zener [5], associated to strong electron-phonon interaction, known as the Jahn-Teller effect [6]. Deficiencies in A-site of the perovskite structure lead to an increase in the Mn^{4+} content and to a change in the average ionic radius $<r_A>$ of the A site, which affect the lattice parameters and in particular the Mn-O distances and Mn-O-Mn bond angles. Therefore, the super-exchange interactions can be enhanced, leading to a decrease of T_C [7]. The present study is a continuation of our lab systematic investigations on the effect of a cationic vacancy in the A-site upon the physical properties of manganese oxides [8–10]. In this context, Boujelben et al. [10] have shown that $Pr_{0.7}Sr_{0.3}MnO_3$ (30% Mn^{4+}) system, which is ferromagnetic below $T_C=265$ K, undergoes different behaviors depending on the nature of the deficiency. In fact, the Curie temperature (T_C) decreases from 265 to 90 K with Sr-vacancy creation; and it shifts to higher temperatures (from 265 to 320 K) while introducing a deficit on Pr. Experimentally, the introduction of a lacuna on either divalent or trivalent ion affects considerably the physical properties, and essentially the Curie temperature [11–16].

The origin of the observed behavior is still not fully understood. Particularly, it is unclear how the magnetic interactions are renormalized near the PM-FM transition range and what universality class governs the PM-FM transitions in these systems. The research on the nature of the phase transitions in magnetic materials has been and still remains one of the present directions in the condensed state physics. Earlier studies on the critical behaviors around the Curie temperature T_C have indicated that critical exponents play important roles in elucidating interaction mechanisms near T_C. The critical behavior in the double exchange model was first described with long-range mean field theory. However, the 3D-Heisenberg model is extensively used to

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understand short-range interaction in doped manganites [17–19]. Furthermore, the interpretations of a few relevant experimental results pertaining to the critical exponents and the universality class of manganites are still controversial.

In this work, we investigate the critical phenomena, based on different techniques including the modified Arrott plott, Kouvel-Fisher method and critical isotherm analysis in $La_{0.6}Ca_{0.2}Ba_{0.15}\square_{0.05}MnO_3$ manganite, where the relevant disorder introduced by the vacancy plays an important role on the magnetic properties. The Curie temperature as well as the critical β, γ and δ exponents were determined and a scaling analysis was used for the test. Moreover, the field dependence of the magnetic entropy change was analyzed through a power law to get a deeper insight on the magneto-caloric effect and to examine the critical exponents and their influence on our compound.

To our knowledge, only few reports were devoted to the critical behavior of lacunar manganese oxides [2], and as we are interested in applications in the field of magnetic refrigeration, a T_C near room temperature is required.

2. Experimental details

$La_{0.6}Ca_{0.2}Ba_{0.15}\square_{0.05}MnO_3$ sample was prepared from high purity La_2O_3, $CaCO_3$, $BaCO_3$ and MnO_2 powders (Aldrich 99.9%) using the conventional solid state reaction. The powders combined with stoichiometric quantities were mixed, ground carefully, and pre-annealed at 800 °C for 24 h. Then, the mixtures were re-ground, pressed into pellets of 13 mm diameter and 2 mm thickness and sintered in air at 900 °C and 1200 °C for 48 h to ensure a better crystallization. Finally, these pellets were cooled slowly to room temperature in air.

Phase purity, homogeneity, and cell dimensions were determined by powder X-ray diffraction(XRD) analysis at room temperature using a 'Panalytical X'Pert Pro' diffractometer with Cu-Kα radiation (λ = 1.5406 A°). The XRD patterns were collected in the range of $10° < 2\theta < 100°$ and the data were analyzed by the Rietveld method using the FULLPROF program. Infrared absorption spectra were measured by Spectrum Two FT-IR Spectrometer in the 700–400 cm^{-1} wave number range at room at room temperature.

Magnetic measurements were carried out using a vibrating sample magnetometer (VSM) J3590 mini CFM of Cryogenics installed in the Digital research Center of Sfax, operating between 4 and 400 K with applied magnetic field up to 5 T. Magnetizations M(T) curves were obtained under 0.05 T. We measured the magnetization versus applied magnetic field in a temperature range near T_C. To extract the critical exponents of the samples accurately, isothermal magnetization data as function of magnetic field were performed in the range of 0–5 T, in the vicinity of the PM to FM phase transition.

3. Results and discussions

3.1. Chemical analysis

Our sample has been elaborated in air; they are consequently stoichiometric in oxygen [20]. A vacancy in the A site implies a partial conversion of Mn^{3+} to Mn^{4+}. The Mn^{4+} content in our sample has been checked by chemical analysis. We list in Table 1 the chemical analysis results. The experimental analysis results show that the Mn^{4+} content for our sample is slightly smaller than the theoretical value. The ratio Mn^{4+}/Mn^{3+} is equal to 0.99 for $La_{0.6}Ca_{0.2}Ba_{0.15}\square_{0.05}MnO_3$ sample.

Table 1
Chemical analysis results for $La_{0.6}Ca_{0.2}Ba_{0.15}\square_{0.05}MnO_3$ compound.

Parameters	$La_{0.6}Ca_{0.2}Ba_{0.15}\square_{0.05}MnO_3$
(%) Theoretical content	
Mn^{3+}	50
Mn^{4+}	50
Mn^{4+}/Mn^{3+}	1
(%) Experimental content	
Mn^{3+}	50.15
Mn^{4+}	49.85
Mn^{4+}/Mn^{3+}	0.99

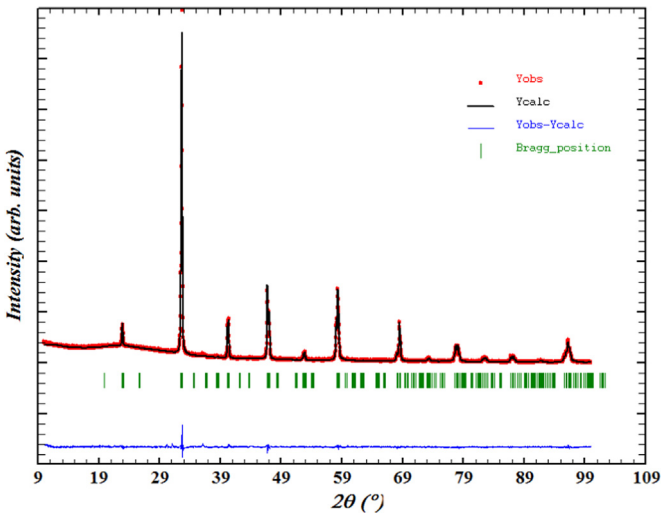

Fig. 1. Full profile fitting of XRD spectrum for $La_{0.6}Ca_{0.2}Ba_{0.15}\square_{0.05}MnO_3$ sample. Squares indicate the experimental data and the calculated data is the continuous line overlapping them. The lowest curve shows the difference between experimental and calculated patterns. The vertical bars indicate the expected reflection positions.

3.2. XRD results

Fig. 1 shows the X-ray diffraction study of the $La_{0.6}Ca_{0.2}Ba_{0.15}\square_{0.05}MnO_3$ compound at room temperature. The data were refined by the Rietveld technique using the Fullprof program. The XRD shows that our sample is single phase without any detectable impurity and can be indexed in the orthorhombic structure with Pbnm space group. The quality of the refinement was evaluated though the goodness of the fit indicator χ^2. A good fit between the observed and the calculated profiles was obtained. Detailed results of the structural refinements, such as the unit cell volume, atomic parameters and other fitting parameters are computed and given in Table 2.

In the perovskite structure, the tolerance factor is relative to the available space in the center of the oxygen octahedron. It is connected to the dimensions of ions of concern and to the distances between them. Perovskite structure can be characterized by this tolerance factor t, defined by the following equation:

$$t = \frac{d_{A-O}}{\sqrt{2}\, d_{B-O}} \quad (1)$$

where $d_{A\text{-}O}$ is the distance between the rare earth and the nearest oxygen while $d_{B\text{-}O}$ is the distance between the oxygen atom and the atom of manganese. The value, t = 0.88, has been estimated and is within the range of stable perovskite structure.

The average crystallite size can estimated from the XRD data using the Scherrer relation as follow [21]