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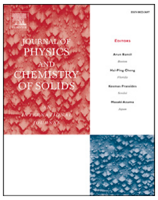

A-site deficiency effects on the critical behavior of $La_{0.6}Ca_{0.15}\cdot_{0.05}Ba_{0.2}MnO_3$

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ABSTRACT

The aim of the present work is to study the critical behavior of calcium deficient $La_{0.6}Ca_{0.15}\cdot_{0.05}Ba_{0.2}MnO_3$ (LCBMO), synthetized by the conventional solid-state reaction method, around the paramagnetic (PM)-ferromagnetic (FM) phase transition. X-ray diffraction revealed that these manganites crystallized in the orthorhombic structure with Pbnm space group. Then, the magnetic properties of this compound are discussed in detail, building on the magnetization and the susceptibility. The temperature dependence of magnetic susceptibility at higher temperature confirms the presence of the Griffiths phase above the Curie temperature which proves the existence of ferromagnetic clusters in the paramagnetic domain. Experimental results revealed that our sample exhibit a second-order magnetic phase transition. The estimated critical exponents derived from the magnetic data were estimated using various techniques such as modified Arrott plot, Kouvel-Fisher method, and critical magnetization isotherms $M(T_C, H)$. The obtained values are very close to those representative of the mean-field model ($\beta = 0.547$, $\gamma = 1.23$, and $\delta = 3.092$ at an average $T_C = 201.74$ K).

1. Introduction

Extensive studies on normal state properties of manganites with perovskite structure with the general formula $Ln_{1-x}A_xMnO_3$ (Ln is a trivalent rare earth and A is a divalent alkaline earth) have attracted a great interest since the discovery of a large negative magneto resistance in these materials [1]. The perovskite structure generally shows lattice distortion from the cubic structure to orthorhombic or rhombohedral ones. This distortion is mainly due to the Jahn-Teller (JT) effect, inducing the deformation of the MnO_6 octahedron. It has been noted that cooperative JT distortions are present in the orthorhombic phase, but not allowed in the rhombohedral one due to a higher symmetry of MnO_6 octahedra [2,3]. Such compounds exhibit a paramagnetic (PM) to ferromagnetic (FM) transition with decreasing temperature [4,5]. Accordingly, the Mn^{3+}-Mn^{4+} ferromagnetic interaction in these manganites strongly depends on both the average bond length <Mn—O>, and bond angle <Mn—*O*—Mn>. The ferromagnetic interaction in these compounds is mediated by the so called double-exchange (DE) mechanism between the Mn^{3+} and Mn^{4+}ions [6,7]. The Curie temperature T_C and the magneto resistance effects are optimized when 33% of the Mn^{3+} is converted into Mn^{4+} by substituting the rare earth with a divalent element [8–10]. However, the theory can only partly explain the magnetic properties and electronic transport in these strongly correlated materials because many distinct deviations from the above DE and JT theory have been found in experiments [11,12]. For this reason, it is necessary to investigate in details the critical exponents around the PM-FM transition. Critical exponents for manganites show wide variation that covering most all universality classes and different experimental tools are used to determine them [13]. Until now, four kinds of different theoretical models which are the mean-field ($\beta = 0.5$, $\gamma = 1.0$ and $\delta = 3.0$), the three dimensional (3D) Heisenberg ($\beta = 0.365$, $\gamma = 1.336$ and $\delta = 4.8$), the 3D-Ising ($\beta = 0.325$, $\gamma = 1.24$ and $\delta = 4.82$), and the tri-critical mean field ($\beta = 0.25$, $\gamma = 1.0$ and $\delta = 5.0$) models were used to explain the critical properties in manganites [14,15]. The experimental estimates for critical exponents in manganites have yielded a wide range of values including those of the short-range Heisenberg interaction [16], the mean-field values [17] and those, which cannot be classified into any universality class [18]. 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 manganites (magnetic and transport properties) [19–21]. In this paper, we focus on the critical behavior of $La_{0.6}Ca_{0.15}\cdot_{0.05}Ba_{0.2}MnO_3$ polycrystalline sample, using the isothermal magnetization, near ferromagnetic-paramagnetic phase transition and show the effect of relevant disorder introduced by vacancy in the

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universality class of $La_{0.6}Ca_{0.15}\cdot_{0.05}Ba_{0.}MnO_3$ manganites. The choice of the deficiency in the A-site is due to the fact that the vacancies enhance the disorder effect in this material. The critical exponents β, γ and δ associated with the second order transition have been determined based on various approaches including the modified Arrott plots, the Kouvel-Fisher method and the critical isotherm analysis. Using these exponents, it has also been verified that the scaling hypothesis is perfectly obeyed indicating that they are reliable.

2. Experimental details

$La_{0.6}Ca_{0.15}\cdot_{0.05}Ba_{0.2}MnO_3$ sample was elaborated using the conventional solid-state reaction. Stoichiometric amounts of La_2O_3, $CaCO_3$, $BaCO_3$ and MnO_2 (purities up to 99.99%) were firstly mixed and ground in an agate mortar then heated at 800 °C for 24 h after an intermediate grinding, they are reacted at 1000 °C for 48 h. Then, a final sintering was carried out at 1200 °C for 48 h. 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 $10° \le 2\theta \le 100°$ angular range with a step of 0.02°. Infrared absorption spectra were recorded at room temperature by a Spectrum Two FT-IR Spectrometer in the 350-700 cm^{-1} wave number range. The magnetic measurements were carried out using a vibrating sample magnetometer (VSM) J3590 mini CFM of Cryogenics. 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. Results and discussion

The phase identification and the structural analysis of $La_{0.6}Ca_{0.15}\cdot_{0.05}Ba_{0.2}MnO_3$ compound was carried out using the X-ray diffraction patterns recorded at room temperature (Fig. 1). We have refined the structure by the Rietveld method [22] using the Fullprof program [23]. The refinement shows that the sample crystallized in the orthorhombic structure with Pbnm space group (Z = 4) without any secondary phase. The lattice parameters, the unit cell volume, and the bond angle <Mn—*O*—Mn> of our sample are summarizing in Table 1. These results are in agreement with those reported in the literature [24].

The average crystallites size (D_{SC}) was calculated from the XRD peaks using the Scherer formula [25].

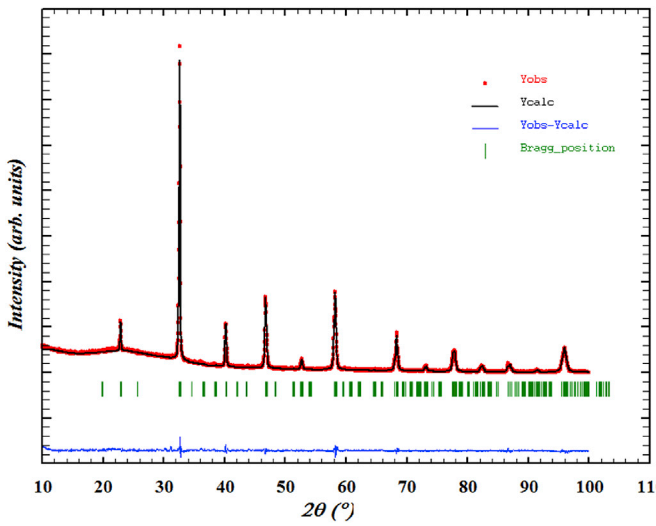

Fig. 1. Observed (symbols) and calculated (solid lines) X-ray diffraction pattern for $La_{0.6}Ca_{0.15}\cdot_{0.05}Ba_{0.2}MnO_3$. Positions for the Bragg reflection are marked by vertical bars. Differences between the observed and the calculated intensities are shown at the bottom of the diagram.

Table 1
The refined structural parameters for $La_{0.6}Ca_{0.15}\cdot_{0.05}Ba_{0.2}MnO_3$ of X-ray diffraction data at room temperature.

$La_{0.6}Ca_{0.15}\cdot_{0.05}Ba_{0.2}MnO_3$	Pbnm space group
a (Å)	5.485 (5)
b (Å)	5.510 (7)
c (Å)	7.746 (6)
V (Å^3)	234.171 (6)
<Mn—*O*—Mn> (°)	164.966 (6)

$$D_{SC} = \frac{K\lambda}{\beta\cos(\theta)} \tag{1}$$

where K = 0.9 is the shape factor, λ is the wave-length of the used X-ray, θ and β are the diffraction angle and the full width of the most intense peak [25]. The average crystallites size D_{SC} was found to be about 38.95 nm.

According to Williamson-Hall (WH) method [26], the individual contributions to the broadening of reflections can be expressed as:

$$\beta \cos\theta = \frac{K\lambda}{S_{WH}} + 4\varepsilon \sin\theta \tag{2}$$

where $\varepsilon = \frac{4d}{d}$ is a coefficient related to strain effect on the crystallites. The value of ε is calculated from the slope of βcosθ vs. 4sinθ plot. It is mostly the correction of Scherrer's formula by taking the strain into account. The 2θ range of 10–100° were used to construct a linear plot of βcosθ vs. 4sinθ (Fig. 2), from which the average crystallites size and the strain were calculated using Eq. (2) and the obtained values are 24.64 nm and 0.05 respectively.

Fig. 3 shows the FT-IR spectra of $La_{0.6}Ca_{0.15}\cdot_{0.05}Ba_{0.2}MnO_3$ compound. The infrared spectra is characterized by a band due to the stretching mode, ν_s, around 562.5 cm^{-1} involving the internal motion of the Mn ion against the MnO_6 octahedron due to the Jahn-Teller effect and a bending mode, ν_b, around 425.5 cm^{-1} which is sensitive to the Mn—*O*—Mn bond angle [27,28].

Fig. 4 shows the temperature dependence of the magnetization M(T) under a magnetic applied field of 0.05 T for our sample. The curve revealed that the LCBMO undergoes a paramagnetic (PM)-ferromagnetic (FM) transition with decreasing temperature. The Curie temperature T_C was determined from dM/dT versus temperature shown in the inset of Fig. 4.

The Curie temperature T_C is found to be 202 K. The calcium vacancy in our sample involves a partial conversion of Mn^{3+} to Mn^{4+} ions according to the formula $La^{3+}_{0.6}Ca^{2+}_{0.15\text{-}x}\cdot^{0}_{x}Ba^{2+}_{0.2}{Mn^{3+}}_{0.6\text{-}2x}{Mn^{4+}}_{0.4+2x}O^{2-}_{3}$, and leads to an increase of Mn^{4+} content, which produces a decrease in the

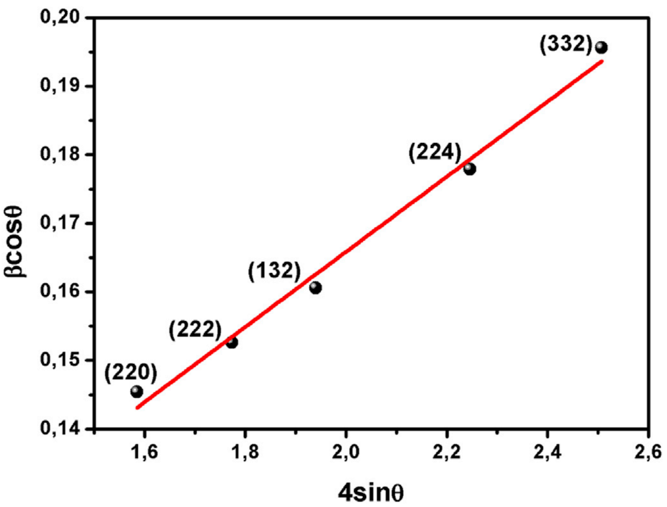

Fig. 2. Williamson-Hall analysis plots of $La_{0.6}Ca_{0.15}\cdot_{0.05}Ba_{0.2}MnO_3$.