Journal of Alloys and Compounds 627 (2015) 211–217

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Influence of magnetic field on the critical behavior of $La_{0.7}Ca_{0.2}Ba_{0.1}MnO_3$

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ARTICLE INFO

Article history:
Received 21 October 2014
Received in revised form 3 December 2014
Accepted 5 December 2014
Available online 25 December 2014

Keywords:
Doped manganite
Magnetic transition
Critical behavior

ABSTRACT

The influence of the magnetic field on the nature of the ferromagnetic phase transition as well as the critical behavior of $La_{0.7}Ca_{0.2}Ba_{0.1}MnO_3$ polycrystalline have been studied systematically. Analysis of the Landau–Lifshitz coefficients obtained from Arrott plots showed that $b(T)$ changes from positive to negative values in different magnetic field ranges, indicating that the behavior cannot be described within a single model under the application of a field. The Kouvel–Fisher method, revealed that the critical exponents obtained for $La_{0.7}Ca_{0.2}Ba_{0.1}MnO_3$ strongly depend on the choice of the field range. The β value shifts from the tricritical mean field model to that consistent with short range 3-D Ising model. For the highest field range of 4–5 T, its approaching again the tricritical model. The γ values are still close to that expected for the mean field model with a slight decrease. These results support evidence of the influence of magnetic field on the coexistence of short- and long-range FM order in $La_{0.7}Ca_{0.2}Ba_{0.1}MnO_3$. The coexistence of short- and long-range FM order is generated from the magnetic inhomogeneity in the sample, which is attributed to the existence of Ca^{2+} and Ba^{2+} rich regions.

1. Introduction

Hole doped rare earth manganites of $R_{1-x}A_xMnO_3$ (R = rare earths, A = alkaline earth or alkali elements) draw the attention of researchers due to of their interesting electrical, transport and magnetic properties [1,2]. The close relation between these properties (e.g. the relationship between the metal–insulator (MI) transition and paramagnetic–ferromagnetic (PM–FM) transition) in these materials has continued to generate interest and reveal new insights, essentially due to the complexity of the systems [3–5]. It has been experimentally shown that the parent compound $RMnO_3$ is an insulating antiferromagnet and the substitution of the trivalent R^{3+} ion by divalent A^{2+} ion, with sufficiently high doping levels (x), leads to the coexistence of Mn^{3+} and Mn^{4+} ions and the material becomes a conductive ferromagnet [6]. It is also known that the crystal structure and the conduction bandwidth of Mn^{3+} itinerant electrons in doped manganites could be easily modified by changing the average radius of ions located at the R/A site. Manganite compounds with a large R/A-site ionic radius have a wide bandwidth and the metallic ferromagnetic state in these compounds was widely interpreted using the double-exchange (DE) mechanism [7]. Meanwhile, those with a small R/A-site ionic radius could be classified into narrow-bandwidth manganites and the metallic ferromagnetic state was explained by other effects such as Jahn–Teller (JT) distortions and coexistence of antiferromagnetic (AFM) interactions with the ferromagnetic phase [8]. The PM–FM transition is of second order in materials with wide bandwidth and it is of first order in narrow-bandwidth compounds. For example, the low critical exponent ($\beta = 0.14$) identified in $La_{0.7}Ca_{0.3}MnO_3$ with a narrow-bandwidth system suggested that the PM–FM transition is of first order rather than second order [9]. On the other hand the study of $La_{0.73}Ba_{0.27}MnO_3$ which is classified in wide bandwidth manganites showed that the transition in this material is a second order one and falls into the universality class of the nearest-neighbor, (3D) Heisenberg model [10]. The change in the nature of the phase transition is also influenced by an applied magnetic field [11]. So, to get more insight into manganite with Ca and manganite with Ba, we prepared $La_{0.7}Ca_{0.2}Ba_{0.1}MnO_3$, and then studied the impact of magnetic field in critical behavior around its FM–PM phase transition temperature.

The partial substitution of Ba^{2+} with a large ionic radius (1.47 Å) for Ca^{2+} (1.18 Å) and La^{3+} (1.216 Å) leads to a large ionic-size mismatch (σ^2) as compared with $La_{0.7}Ca_{0.3}MnO_3$. The σ^2 value of $La_{0.7}Ca_{0.2}Ba_{0.1}MnO_3$ is about 1.67×10^{-2}. Such structural modification coupled with the variation of field influence the FM interaction between Mn^{3+} and Mn^{4+} ions.

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http://dx.doi.org/10.1016/j.jallcom.2014.12.020
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2. Experimental

Polycrystalline perovskite manganite $La_{0.7}Ca_{0.2}Ba_{0.1}MnO_3$ was prepared by sol–gel method. Stoichiometric amounts of La_2O_3, $CaCO_3$, $BaCo_3$ and MnO_2, were dissolved in a concentrated nitric acid to transform them into nitrate. In order to accelerate the dissolution the solution was well magnetically stirred at 60 °C. After reaching total dissolution, suitable amounts of citric acid (CA) was added as the complexation agent (1.5 mol of citric acid corresponds to 1 mol of metal cation). After that we add the ethylene glycol (EG) as a chelating agent. Then, the temperature was slowly increased to 80 °C under constant stirring to evaporate the excess solvent and to accelerate the poly-esterification reaction between CA and EG. When the solvent in the system was completely evaporated, a homogeneous red resin with a glassy appearance was obtained. This resin was then dried at 150 °C overnight to evaporate a nitrogen element and obtain a black fine powder which was then crushed and heated in air at 300 °C before sintering at various temperatures (400–800 °C) for 6 h. After cooling, the sample was pressed into a pellets (of about 1 mm thickness and 13 mm diameter), and then sintered at 1000 °C for 24 h in air. Phase purity of the sample was verified by X-ray powder diffraction (XRD). The structural parameters of the sample are refined by Rietveld's profile-fitting method [12]. It has been found that the sample can be indexed in the orthorhombic structure with Pbnm space group (Fig. 1). A SEM image of the $La_{0.7}Ca_{0.2}Ba_{0.1}MnO_3$ sample is shown inset Fig. 1. We observe that various sizes of grains are randomly distributed and there is a low intergrain porosity. The average grain size of the particle is about 90 nm. The magnetization measurements were performed using a vibrating sample magnetometer.

3. Results

Fig. 2 shows the temperature dependence of magnetization obtained under an applied field of 0.05 T for $La_{0.7}Ca_{0.2}Ba_{0.1}MnO_3$ sample. The sample undergoes a PM–FM transition at $T_C = 233$ K estimated from the temperature dependence of the differential quotient of magnetization dM/dT as shown in inset of Fig. 2. It can be found that the Curie temperature of $La_{0.7}Ca_{0.2}Ba_{0.1}MnO_3$ sample is slightly higher than that of $La_{0.7}Ca_{0.3}MnO_3$ sample, indicating the overall exchange interaction between Mn^{3+} and Mn^{4+} ions in the former is stronger than that in the later. It is well known that the sharpness of the magnetic transition and magnetic homogeneity are strongly sample morphology-dependent [13–15].

Fig. 3(a) shows the M vs. H plots in the temperature range $T_C \pm 20$ K with a temperature step of 2 K. These curves exhibit a gradual ferromagnetic (FM)-to-paramagnetic (PM) transition. The magnetization saturation is not fully reached. This behavior, also observed in other compounds, is characteristic of samples without true long-range-order ferromagnetism [16,17]. Fig. 3(b) shows the Arrott plot M^2 vs. H/M ($\beta = 0.5$, and $\gamma = 1$). According to the criterion proposed by Banerjee, the positive slopes of the M^2 vs. H/M plot suggest a second order transition in this system [18].

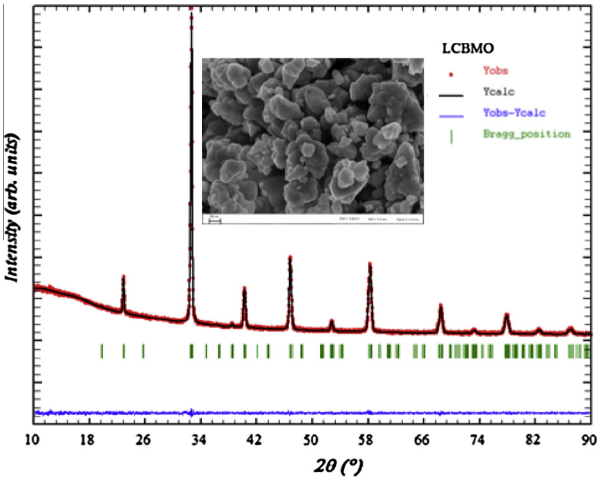

Fig. 1. XRD patterns of $La_{0.7}Ca_{0.2}Ba_{0.1}MnO_3$: squares indicate the experimental data and the calculated data is the continuous line overlapping them. The lowest curve shows the difference between experimental and calculated pat-terns. The vertical bars indicate the expected reflection positions.

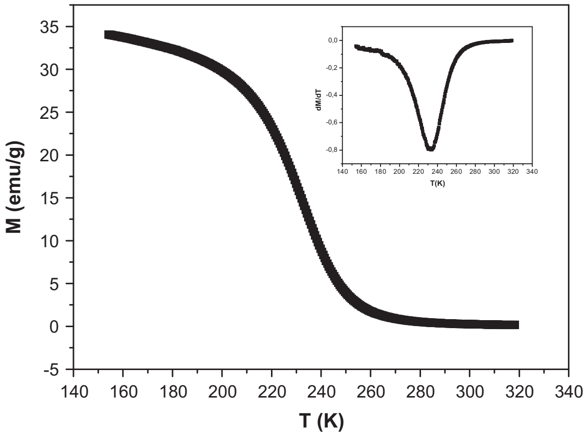

Fig. 2. Temperature dependence of magnetizations at 0.05 T for $La_{0.7}Ca_{0.2}Ba_{0.1}MnO_3$ sample. The inset shows dM/dT vs. T.

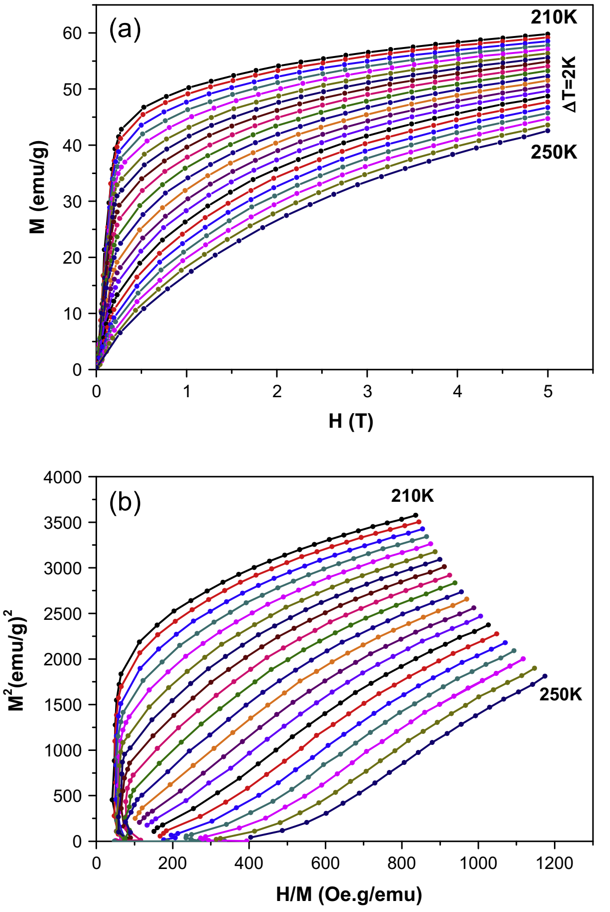

Fig. 3. (a) $M(H)$ curves and (b) Arrott plots for $La_{0.7}Ca_{0.2}Ba_{0.1}MnO_3$ sample at different temperatures.

In the Landau–Lifshitz theory, the equation of state can be expressed as

$$H = a(T)M + b(T)M^3 + \dots \quad (1)$$

where $a(T)$ is related to the inverse of the magnetic susceptibility and reaches a minimum (~ 0) at T_C. The sign of $b(T)$ – the slope of (H/M) vs. M^2 – is an indication of the order of the magnetic transi-