



# Critical properties around the ferromagnetic–paramagnetic phase transition in $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{A}_x\text{MnO}_3$ compounds ( $\text{A} = \text{Sr}, \text{Ba}$ and $x = 0, 0.15, 0.3$ )



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## ABSTRACT

Influence of alkaline earth element doping in the A-site on the structure, magnetic and magnetocaloric properties of  $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{A}_x\text{MnO}_3$  ( $\text{A} = \text{Sr}$  and  $\text{Ba}$ ;  $x = 0, 0.15$  and  $0.3$ ) perovskite manganites have been investigated. X-ray diffraction data indicates that samples  $x = 0$  and  $0.15$  crystallize in the orthorhombic structure (space group  $Pnma$ ), whereas samples  $x = 0.3$  belong to the rhombohedral structure (space group  $R-3c$ ). Substitution of Sr or Ba for Ca plays an important role in the increase of Curie temperature ( $T_C$ ) and modification the nature of the magnetic phase transition in materials. Sample  $x = 0$  exhibits the first-order phase transition (FOPT) with a large magnetic entropy change ( $\Delta S_m$ ), whereas samples  $x = 0.15$  and  $0.3$  exhibit the second-order phase transition (SOPT) characterizations and the moderate values of  $\Delta S_m$ . Using the modified Arrott plots method, the critical behaviors around  $T_C$  for SOPT samples have been investigated through the values of critical parameters ( $T_C$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ ). We pointed out that Ba-doping favors establishing long-range ferromagnetic order, contrary to the case of Sr-doping.

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## 1. Introduction

In the past few decades, perovskite-type manganites ( $\text{ReMnO}_3$  with Re is a rare-earth element;  $\text{ABO}_3$  type) have attracted considerable interest due to their complex magnetic and transport properties. Though  $\text{ReMnO}_3$  is an antiferromagnetic (AFM) insulator, substituting the Re-site by a alkali earth or alkali elements (A) in order to formula  $\text{Re}_{1-x}\text{A}_x\text{MnO}_3$  compound leads to number of  $\text{Mn}^{3+}$  ( $t_{2g}^3 e_g^1$ ,  $S = 2$ ) ions with ionic radius  $r_{\text{Mn}^{3+}} = 0.645 \text{ \AA}$  to be converted to  $\text{Mn}^{4+}$  ( $t_{2g}^3$ ,  $S = 3/2$ ) ions with smaller ionic radius ( $r_{\text{Mn}^{4+}} = 0.53 \text{ \AA}$ ) and mobile  $e_g$  electrons are introduced. Thus material becomes a metallic ferromagnet and exhibiting the

ferromagnetic (FM)-paramagnetic (PM) phase transition at the Curie temperature ( $T_C$ ). The magnetic and transport properties of  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  ( $\text{A} = \text{Ca}, \text{Sr},$  and  $\text{Ba}$ ) compounds have been investigated since the 1950s, which can be found elsewhere [1–3]. It was shown that the physical properties of materials will be changed by substitution of  $\text{La}^{3+}$  by a divalent ion. Changing the rate of substitution, the materials can be either FM or AFM, and insulating, semiconducting or even metallic. Thus, the materials exhibit a variety of physical properties, such as the colossal magnetoresistance (CMR) effect and the magnetocaloric effect (MCE) [4,5]. Basically, magnetic and electrical properties in manganites are frequently explained base on the double exchange (DE) mechanism, where electron transports from  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  via an oxygen ion, which were proposed by Zener [6]. It has been shown that the magnetic and transport properties of  $\text{Re}_{1-x}\text{A}_x\text{MnO}_3$  are strongly affected by the Mn–O bond length and Mn–O–Mn bond angle controlled by the Re/A-site ions radii and  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio which modifies the

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DE and the super exchange (SE) interactions [4,5]. The reports also shown the CMR and the MCE in manganites can be easily tuned by doping some chemical elements into the sites of Re (or A) and Mn. Among hole-doped manganites,  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  compounds with  $x = 0.3$  (corresponding to  $\text{Mn}^{3+}/\text{Mn}^{4+} = 7/3$ ) usually show the strongest physical effects [4,5]. With this  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio, the  $\text{Mn}^{3+}\text{-Mn}^{4+}$  FM DE interactions are dominant in comparison with the AFM SE interactions of  $\text{Mn}^{3+}\text{-Mn}^{3+}$  and  $\text{Mn}^{4+}\text{-Mn}^{4+}$  pairs. In contrast, the AFM SE interactions are dominant, and thus depress the FM DE interactions in the materials with  $x > 0.3$  and  $x < 0.3$  [4]. However, it is well known that the DE and the SE interactions between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions alone cannot explain all the behaviors observed in manganites. Thus, many studies suggest that it is rely on strong electron-phonon interaction known as the Jahn-Teller effect [7,8], the average Re-site cationic radius [9,10], and the oxygen deficiency [11], etc. However, the origin of the observed properties is still not fully understood. Among these, the magnetic interactions near the FM-PM transition region are still a controversial issue and what universality class governs the FM-PM transitions in the manganites [12–29].

To better understand the nature of the magnetic interactions near the FM-PM phase transition, it is important to study in detail the critical exponents associated with the FM-PM transition. The critical behavior in the double exchange interaction was first described by the long-range mean-field theory (MFT) [30]. In 2000, Motome and Furulawa suggested that the critical behavior should be attributed to the short-range 3D-Heisenberg model [31]. Consequently, the experimental estimates are still controversial concerning the critical exponents and even the order of the magnetic transitions including the 3D-Heisenberg, the 3D-Ising, the mean-field models and those cannot be classified into any universality class ever known [32]. Basically, the FM-PM phase transition of  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  polycrystalline and single-crystal bulks has been known as a first-order phase transition (FOPT) [21,33–35]. For  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ -nanostructured samples, the samples with particle sizes higher than a critical particle size (around 95 nm) undergo the FOPT [36]. In contrast, Taran et al. [12] reported that the polycrystalline  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  undergoing a second-order phase transition (SOPT) with the critical exponents  $\beta = 0.36$  and  $\gamma = 1.2$ , which are close to those expected for the 3D Heisenberg model ( $\beta = 0.365$  and  $\gamma = 1.386$  [30]). Meanwhile, Shin et al. [13] obtained  $\beta = 0.14$  and  $\gamma = 0.81$  in the  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  single-crystal, they suggested that the FM-PM transition in this sample is a FOPT rather than a SOPT type. Recently, Zhang et al. [37] has shown that the FM-PM transition in the  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  system with  $0.2 \leq x \leq 0.4$  follows a second-first-second order progression. While various other manganites (e.g.  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  and  $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ ) exhibit as the SOPT materials [12,14–20,38–42]. However, the experimental values of the critical exponents for these compounds do not converge. Their  $\beta$  and  $\gamma$  values implied that the materials do not belong to a single universality class.

In this paper, we have investigated the influence of various alkaline earth elements on the magnetic interactions of  $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{A}_x\text{MnO}_3$  compounds with  $\text{A} = \text{Sr}$  and  $\text{Ba}$ ;  $x = 0, 0.15$ , and  $0.3$ . A detailed analysis and comparison about critical behaviors of manganites with a ratio  $\text{Mn}^{3+}/\text{Mn}^{4+} = 7/3$  have been presented. We point out that for all the samples undergoing a SOPT, except for  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  compound undergoing a FOPT. Further, the long-range order FM was observed in  $\text{La}_{0.7}\text{Ca}_{0.15}\text{Sr}_{0.15}\text{MnO}_3$ ,  $\text{La}_{0.7}\text{Ca}_{0.15}\text{Ba}_{0.15}\text{MnO}_3$ , and  $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$  compounds with critical exponents are very close to those expected for the mean field theory model ( $\beta = 0.5$  and  $\gamma = 1.0$  [30]). In contrast, the value  $\beta = 0.382$  and  $\gamma = 1.160$  obtained for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  compound suggests this compound following the short-range 3D-Heisenberg [30]. Additionally, we have constructed the universal master curve, which

was proposed by Franco and Code [43], for all the temperature dependences of magnetic entropy change,  $\Delta S_m(T)$ , under different applied magnetic field changes ( $H$ ) of the samples.

## 2. Experimental

Five polycrystalline  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  (LC),  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LS),  $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$  (LB),  $\text{La}_{0.7}\text{Ca}_{0.15}\text{Sr}_{0.15}\text{MnO}_3$  (LCS) and  $\text{La}_{0.7}\text{Ca}_{0.15}\text{Ba}_{0.15}\text{MnO}_3$  (LCB) samples were prepared by a solid state reaction method, used high-purity powders (99.9%) of  $\text{La}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{BaCO}_3$ , and Mn metal as precursors. These powders combined with stoichiometric masses were ground and mixed, and then calcinated at  $1200^\circ\text{C}$  for 24 h in air. The obtained mixtures were re-ground and pressed into pellets. These pellets were finally sintered at  $1400^\circ\text{C}$  for 24 h in air. The crystal structure of the final products was checked by an X-ray diffractometer (SIEMENS-D5000) equipped with the  $\text{Cu-K}\alpha$  radiation source ( $\lambda = 1.5406 \text{ \AA}$ ). Using the redox titration method (using  $\text{K}_2\text{Cr}_2\text{O}_7$  titrant and  $\text{C}_{24}\text{H}_{20}\text{BaN}_2\text{O}_6\text{S}_2$  as the colorimetric indicator) to estimate the stoichiometric oxygen in the samples. Our results show the insignificant oxygen deficiencies or excesses (smaller than 0.005) in all the samples. Therefore, we consider the oxygen concentration in these samples is kept stoichiometric. The magnetization measurements versus temperature and magnetic field,  $M(T, H)$ , were performed on a vibrating sample magnetometer (VSM) according to the increasing direction of temperature intervals of 2 K. The applied magnetic field ( $H_{\text{app}}$ ) has been corrected by a demagnetization factor ( $D$ ) into the internal magnetic field as  $H = H_{\text{app}} - DM$ .

## 3. Results and discussion

Room-temperature X-ray diffraction (XRD) patterns of the samples are showed in Fig. 1. It suggests that all the samples are single phase of  $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{A}_x\text{MnO}_3$  perovskite with  $\text{A} = \text{Sr}$  and  $\text{Ba}$ ;  $x = 0, 0.15$ , and  $0.3$ . Among these, the samples  $x = 0$  and  $0.15$  belonging to the orthorhombic structure, space group  $Pnma$  (Fig. 1(a)), whereas the samples  $x = 0.3$  belonging to the rhombohedral one with space group  $R\bar{3}c$  (Fig. 1(b)). Based on the XRD data, we calculated the lattice parameters ( $a$ ,  $b$ , and  $c$ ) and the volume of unit cell ( $V$ ) as shown in Table 1. The  $V$  value increases when Sr and Ba replacement for Ca due to an enhancement of the average radius of the ions located at A site ( $\langle r_A \rangle$ ) in the perovskite structure  $\text{ABO}_3$ . Accordingly, the lattice distortion is caused by the partial replacement of  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  with the larger ionic radii (1.44 and 1.61 Å, respectively [44]) for  $\text{La}^{3+}$  or  $\text{Ca}^{2+}$  ions with a smaller radius (1.36 or 1.34 Å, respectively [44]) which is governed by the Goldsmid tolerance factor given by Ref. [26],  $t_G = (\langle r_A \rangle + r_O) / \sqrt{2}(\langle r_B \rangle + r_O)$ , where  $\langle r_A \rangle$  and  $\langle r_B \rangle$  are the average radii of the cations located at A and B sites, respectively,  $r_O$  is the radius of oxygen anion in the perovskite structure  $\text{ABO}_3$ .  $t_G$  is the geometric measure of size mismatch of the perovskite. The structure of manganites is of perovskite if their  $t_G$  values lies in the limits of  $0.75 < t_G \leq 1$  and in an ideal case this value is unity. In present case, the  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  replacements do not change the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  content ratio ( $\text{Mn}^{3+}/\text{Mn}^{4+} = 7/3$ ) in the samples, but enhance the values of  $\langle r_A \rangle$  and  $t_G$ , see Table 1. However, the values of  $t_G$  obtained for samples are in the region of 0.969–0.997, one may conclude that all the samples have a stable perovskite structure.

Following the structure analyses, we have investigated the magnetic properties of the samples. As presented in Fig. 2(a), normalized thermo-magnetization curves ( $M/M_{100\text{K}}$  vs.  $T$ ) measured under an applied field of 100 Oe in the zero-field cooled mode for the samples show a sharp FM-PM phase transition. This phase transition is associated with the  $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{A}_x\text{MnO}_3$

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