Physica B: Condensed Matter 541 (2018) 43–49

Contents lists available at ScienceDirect

Physica B: Condensed Matter

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

Role of antimony in the charge transport mechanisms for $La_{0.67}Ca_{0.33}Mn_{1-x}Sb_xO_3$ manganites

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ARTICLE INFO

Keywords:
Ceramics
Substitutional effect
Transport properties
Manganites

ABSTRACT

Single phasic $La_{0.67}Ca_{0.33}Mn_{1-x}Sb_xO_3$ (LCMSO; x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) samples were characterized by performing temperature and magnetic field dependent resistance measurements. Present study, mainly, aims for the better understanding of possible charge conduction mechanisms responsible for the low temperature resistivity and high temperature [well above metal to insulator transition temperature (T_P)] semiconducting regions. Variation in resistivity and T_P with Sb^{5+} content (x) and applied magnetic field has been discussed in the light of the modifications in structural and magnetic lattices of smaller diamagnetic Sb^{5+} doped LCMSO system. Various models and mechanisms have been theoretical employed to fit obtained experimental resistivity data for the low temperature resistivity and semiconducting regions of all LCMSO manganites. It is found that low temperature resistivity minima follows the coulomb blockade model while charge conduction in the semiconducting region obeys the variable range hopping (VRH) mechanism. Variation in low temperature blocking energy, activation energy in semiconducting region and magnetoresistance (MR) with Sb^{5+} content (x) and applied magnetic field has been discussed in detail.

1. Introduction

Most of the attention, up to the date, has been focused on the doping of divalent alkaline earths, e.g. Ca, Ba, Sr and Pb in the parent compound $LaMnO_3$ [1–4]. This is due to the maximum transition temperature exhibited by optimally divalent alkaline earths doped $LaMnO_3$. This also supports the zener double exchange (ZDE) mechanism, thereby, ferromagnetism and conduction in the divalent doped manganites. In addition to ZDE mechanism, manganites are also known to exhibit large change in resistance upon an application of external magnetic field, i.e. MR effect. Such prototype materials, $La_{1-x}A_xMnO_3$ (A = Ca and Sr), also exhibit a very rich phase diagram [5,6] due to which these perovskite oxides become, now a day, very interesting functional materials for many practical applications such as temperature sensors [7], magnetic field sensors [8], electric field sensors [9], p–n junctions [10], capacitors [11], field effect devices [12], composites [13], etc. Since, Ca^{2+} is only a smaller ion than parent La^{3+} ion, as compared to all other three ions (i.e. Sr^{2+}, Pb^{2+} and Ba^{2+}), at low Ca doping ($x < 0.18$), $La_{1-x}Ca_xMnO_3$ are ferromagnetic (FM) insulators, whereas at higher Ca doping ($x > 0.5$), they become antiferromagnetic (AF) insulators. In the intermediate doping range of $0.18 < x < 0.5$, one observes, both, FM and metallic behavior, simultaneously coexist, which leads to CMR near the onset of FM ordering [14,15]. Interestingly, in the AF insulating phase ($x \approx 0.5$), CMR, with a large magnitude, has also been observed [16].

Since the essential degrees of freedom (such as spin, charge, orbital and lattice) are closely linked to the Mn ions, substitutional study at the Mn site is expected to bring about a dramatic effects. A large number of studies have been carried out for the effect of Mn site substitution on the physical properties of different manganite systems [17–29]. Generally, it has been found that possible substitutions by various ions such as 3d transition metals [17–22], Al [23–25], In Ref. [26], Ga [27], Sn [28] and Ge [29] result in the lowering of transition temperatures [i.e. T_P and FM to paramagnetic (PM) (T_C)], but to different extents, and eventually lead to insulating states exhibiting cluster/spin glass properties. The reduction in the T_P/T_C has been broadly attributed to the weakening of the DE interaction strength. No systematic attempts have been made to define the various factors affecting the transition temperatures. It can be understood that, there are at least two major contributions, (i) local structural effects and (ii) local magnetic coupling effects, influencing the transition temperatures of the CMR manganites. Local structural effects

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https://doi.org/10.1016/j.physb.2018.04.031
Received 29 December 2017; Received in revised form 27 March 2018; Accepted 21 April 2018
Available online 24 April 2018

play a dominant role, both, in affecting the phase transition temperatures and in the ground state properties of CMR manganites.

Some studies have been purely devoted to the substitution of Mn ions by high valance Sb^{5+} in different manganite systems [30–34]. Dependence of magnetism, charge transport, thermal conductivity and thermoelectric power of Sb–doped $CaMn_{1-x}Sb_xO_3$ manganites on the hydrostatic pressure has been discussed in detail [30]. Sen et al. [31] have studied the effect of Sb substitution for Mn in $La_{2/3}Ba_{1/3}Mn_{1-x}Sb_xO_3$ ceramic manganites on the structural and magnetoresistive behaviors. Thermoelectric power, thermal conductivity and specific heat measurements were studied for understanding the effect of Sb substitution for Mn–site in $La_{2/3}Ba_{1/3}Mn_{1-x}Sb_xO_3$ manganites on various thermal properties [32]. Recently, interesting magnetic structure has been investigated for Sb–doped $La_{0.6}Sr_{0.4}Mn_{0.8}Sb_{0.2}O_3$ compound using neutron powder diffraction technique [33]. Sb–doping dependent structural, electrical and magnetic properties of $Pr_{2/3}Ba_{1/3}MnO_3$ manganites have been studied in detail [34]. Few reports also exist on the study on various charge conduction mechanisms employed to understand the resistivity behavior of mixed valent manganites substituted with different ions at Mn–site [31,35–37]. Sen et al. [31] have studied the charge transport mechanisms, responsible for the metallic region observed in the resistivity – temperature behavior of $La_{2/3}Ba_{1/3}Mn_{1-x}Sb_xO_3$ ceramic manganites under different applied magnetic fields, using different order of power laws. They have also investigated the charge conduction processes take place in the semiconducting regions of the studied manganites. Rathod et al. [35] have reported the variable range hopping and ZDE mechanisms as govern for conduction in semiconducting and metallic regions, respectively, of Al–doped $La_{0.7}Ca_{0.3}Mn_{1-x}Al_xO_3$ mixed valent manganites. Various models and mechanisms have recently been reported for the understanding of charge conduction in Bi–doped charge ordered mixed valent manganites [36,37].

Keeping in mind all above mentioned aspects of Mn–site substitutional effects in manganites, in this communication, an attempt has been made to understand the effect of Sb^{5+} doping at Mn–site in LCMSO system in modifying the structural lattice distortion due to smaller ion (Sb^{5+}: 0.6 Å) substitution at large ionic Mn–site, variation in Mn valance states due to substitution of higher valance (5 + of Sb at Mn–site results into the reduction in Mn^{4+} ion density) and magnetic Mn lattice modifications (through a magnetic interaction between the Sb and Mn ions. Few aspects of structure–property correlations have already been reported for the presently studied LCMSO system [38–40], while in this extensive report deals with various mechanisms and models as possible sources of charge conduction in metallic and insulating (semiconducting) regions, observed in the temperature dependent resistivity behavior of all LCMSO samples. Also, separate contributions of internal and external parameters to the MR behavior of LCMSO system has been discussed by using complex theoretical expressions.

2. Experimental details

Polycrystalline samples of presently studied LCMSO manganites with x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10 (hereafter referred as S0, S2, S4, S6, S8 and S10, respectively) were synthesized using conventional solid state reaction (SSR) route, as already discussed in Refs. [38–40]. The dried starting powders of La_2O_3, $CaCO_3$, MnO_2 and Sb_2O_5 were mixed in stoichiometric proportions and calcined at 950 °C for 24 h. Samples were then pressed into pellets and sintered at 1050 °C for 48 h followed by a sintering at 1150 °C for 72 h. Oxygen stoichiometry (content) in all the LCMSO samples was confirmed by performing step–by–step chemical processes followed by required calculations as iodometric titration method, reported elsewhere [41]. X–ray diffraction (XRD) patterns were recorded on Philips diffractometer (PW 3040/60, X'pert PRO) using CuKα radiation at RT. Structural analysis was carried out using Rietveld refinement using the standard FULLPROF code [42]. Electrical resistivity and magnetoresistance measurements (temperature range: 5–300 K and field range: 0 – 8 T) were performed using the standard four probe dc method.

3. Results and discussion

Rietveld refinement on the raw data of XRD measurements [38–40] confirms single phasic nature of all the samples understudy as well as no impurity phase or structural phase transformation has been identified within the measurement range studied. Most intense peak gets shifted towards lower 2θ degree and converted into doublet which has been attributed to the substitution of smaller Sb^{5+} (0.6 Å) at larger Mn^{3+} (0.645 Å) site and, hence, enhancement in lattice parameters and unit cell volume. In order to understand the magnetotransport properties of presently studied LCMSO manganite system and to study the substitutional effect of Sb^{5+} on the MR behavior of LCMSO samples, the resistance measurements as a function of temperature has been carried out in the temperature range 5–300 K under 0 and 8 T fields for all the LCMSO samples the plots are shown in Fig. 1. It can be seen that resistivity gets enhanced throughout the temperature range studied while T_P gets suppressed upon increasing Sb^{5+} content (x) in LCMSO system, under both (0 and 8 T) applied magnetic fields. Increase in resistivity and reduction in T_P in LCMSO system can be understood as follow in six different possible aspects: (i) ionic size, valence state, coordination number and structure of Sb^{5+} and $Mn^{3+/4+}$ ions lead us to believe that in the desired six–fold coordination, Sb^{5+} ions (0.60 Å) would replace Mn^{4+} (0.53 Å) rather than Mn^{3+} (0.645 Å) ionic site due to lesser valence difference between Sb^{5+}/Mn^{4+} pair than Sb^{5+}/Mn^{3+} pair, (ii) substitution of smaller Sb^{5+} ions at Mn^{4+} site introduces a structural disorder at B–site in ABO_3 perovskite structure due to a large ionic size difference between them, (iii) magnetic interactions between the magnetic Mn^{3+} and diamagnetic Sb^{5+} come into the picture, (iv) structural disorder result in the modifications in Mn—O—Mn bond angles and Mn—O bond lengths which resulting in the deterioration in e_g electron transfer from Mn^{3+} to Mn^{4+} via O^{2-} and, hence, reduces the transfer integral of itinerant

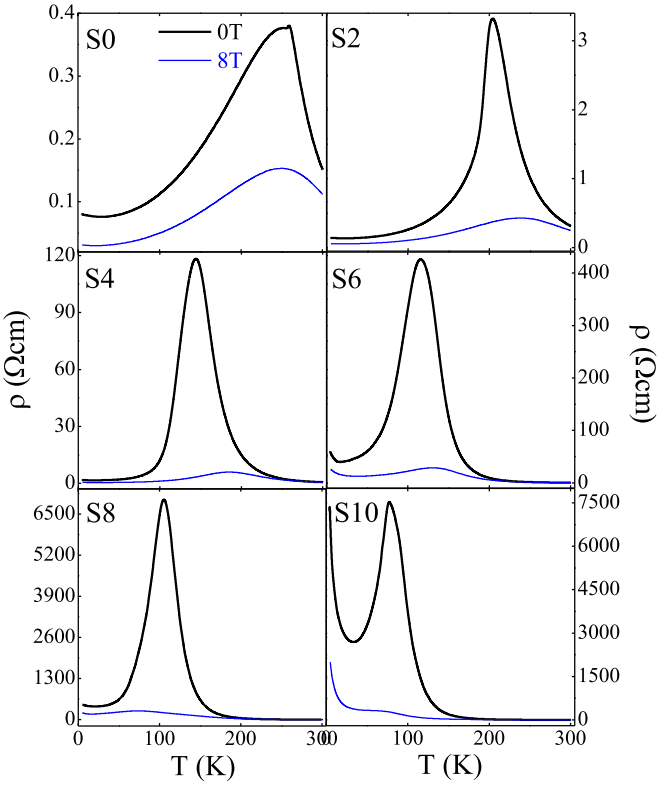

Fig. 1. Variation in resistivity with temperature under various fields (0 and 8 T) for LCMSO manganites.