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# Crystallographic direction dependence of electrical-transport, magneto-transport, magnetic and thermal properties of $La_{0.7}Ca_{0.3}MnO_3$ single crystal

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ABSTRACT

The crystallographic direction dependence of the electrical-transport, magneto-transport, magnetic and thermal properties of $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) single crystal along *c*-axis and *ab*-plane are investigated. The resistivity data shows the metal-insulator transition ($T_{MI}$) occurs at 211 K along *c*-axis and 185 K along *ab*-plane. The electrical resistivity results are investigated by various theoretical models below and above $T_{MI}$. The *dc*-magnetization shows ferromagnetic-paramagnetic transition ($T_C$) at 208 K along *c*-axis and at 190 K along *ab*-plane. Moreover, *ac*-susceptibility and specific heat measurements reveal the phase transition temperature are in close agreement with the resistivity and magnetization measurements. To implement sensor application and data storage capacity, the temperature coefficient of resistance (TCR) and magnetoresistance (MR) are found to ~17% $K^{-1}$ and 98% respectively.



## 1. Introduction

The colossal magnetoresistive (CMR) materials with chemical formula, $RE_{1-x}A_xMnO_3$ (RE-rare earth, A-alkaline earth metals) have attracted much interest over the last few years. In perovskites manganites, $LaMnO_3$ is antiferromagnetic insulator characterized by a super exchange coupling between $Mn^{3+}$ sites facilitated by a single $e_g$ electron which is subjected to strong correlation effects. Partial substitution of $La^{3+}$ ion with divalent cation results in a mixed valance states of Mn ($Mn^{3+}$ and $Mn^{4+}$) and the compound exhibits metal–insulator transition ($T_{MI}$) in which metallic regime is of ferromagnetic nature. Subsequent studies clearly indicated that the CMR phenomenon depends on several factors such as mixed valency, charge ordering, ionic size mismatch, Mn—O bond lengths, Mn—O—Mn bond angles, and oxygen stoichiometry [1–3]. The stability of the perovskite structure depends on the tolerance factor defined by Goldsmith tolerance factor and is formulated as, $t = \frac{(r_A + r_o)}{\sqrt{2}(r_B + r_o)}$ where $r_A$, $r_B$ and $r_O$ being the radii of A cation, B cation and oxygen ion respectively. The perovskite structure is stabilized in the range of $0.75 \leq t \leq 1$. For $t < 1$, the cubic structure transforms to the orthorhombic structure which leads to deviation in Mn—O—Mn bond angle from 180° (an ideal perovskite) leading to the distortion in the $MnO_6$ octahedra. As the tolerance factor decreases, the bandwidth of the itinerant $e_g$ electron decreases and hence reduces $T_C$ (ferromagnetic–paramagnetic transition) and $T_{MI}$.

Depending on the bandwidth of the $e_g$ electron, the manganites can be broadly classified into three major systems: (1) Low bandwidth, (2) Intermediate bandwidth and (3) Large bandwidth systems. The manganite system, $La_{1-x}Ca_xMnO_3$ which exhibits transition below room temperature is an intermediate bandwidth system. The transport properties of the manganites are influenced by distortions generated by the size mismatch at A-site due to the cation of different radii of A-site and also by cationic vacancies of RE (3+) and A (2+) elements which offers a local distortion of the lattice and is given by relation $\sigma^2 = \sum_i x_i r_i^2 + < r_A^2 >$ where, $x_i$ and $r_i$ are fractional occupancy and ionic radius of $i^{th}$ cation at A-site. $<r_A>$ is the average A-site cation radius. The change in ionic radii affects the Mn—O—Mn bond angle and in turn distorts the $MnO_6$ octahedra, which largely affects the electrical transport and magnetic properties in this compound. Therefore, the physical

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properties of the manganites can be tuned either by doping at the RE or Mn-sites in the perovskite structure [4–6]. Extensive applications have been made in the field of magnetic field sensing, magnetic refrigeration, read head devices and bolometric infrared detection devices [7–10]. Among all perovskite manganites, the CMR behavior of doped manganite perovskite $La_{1-x}Ca_xMnO_3$ (LCMO) [11] occurs near the $T_C$ and this remarkable phenomenon is attributed to the magnetic coupling between $Mn^{3+}$ and $Mn^{4+}$ ions as well as to the strong electron-phonon coupling arising from Jahn-Teller splitting of Mn *3d* levels [12]. In order to understand various physical properties of substituted bulk LCMO manganites and their thin films, few proposed mechanisms and theories have been reported and afford high temperature coefficient of resistance (TCR) and magnetoresistance (MR) at room temperature [13,14].

At present, the most common bolometer temperature sensing materials are vanadium oxides ($VO_x$) with TCR above 4%/K and amorphous silicon (a-Si) with TCR up to about 3%/K at room temperature [15,16]. Thin films of $La_{1-x}Ba_xMnO_3$ is a candidate for uncooled bolometer operation and has room-temperature TCR value of 5%/K [17]. Recently Tank et al. [18] have reported high TCR (6.10%) and MR (72%) in LCMO thin film at around room temperature through annealing processing parameter and controlling film thickness. The physical properties of the manganite bulk and thin film are sensitive to structure, oxygen content, and disorder; therefore, the $T_C$ and resistivity of the bulk and film are somewhat different from that of the single crystal. This fact suggests that the physical properties of this compound should be investigated using single crystalline phase. Although, the transport phenomena in La–Ca manganites have been fairly understood, very few attempts have been made to study their properties on single crystals [19–22]. To the best of our knowledge, earlier pressure dependence studies have reported that the compressibility along the *c* axis is different from that of along the *ab* plane in double layered manganites single crystal [23]. It is also reported for superconducting state properties which are sensitive to crystallographic direction dependence pressure studies [24]. The application of uniaxial pressure along *c*-axis and *ab*-plane studied well understood in $Nd_{1-x}Sr_xMnO_3$ single crystal [25]. Due to the strong anisotropic structural, electronic, and magnetic coupling, it is believed that the effect of uniaxial magnetic field on transport properties would be very different from that of pressure.

The manganite crystals of the nominal composition show drastically different magnetic and electric characteristics depending on their point defect structure. Therefore, preparation of high-quality single crystals of manganite is very important. In view of these facts, in the present work we have first time studied the crystallographic direction dependence of transport and magnetic properties of $La_{0.7}Ca_{0.3}MnO_3$ single crystal along both crystallographic planes to understand the role of double exchange mechanism and electron-phonon coupling affects on electrical and magnetic properties. Earlier, no such effort has been made, and hence the present results could not be compared with earlier work. In this context, crystallographic direction dependence of the electrical-transport, magneto-transport, magnetic and thermal properties of the hole doped $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) single crystal along *c*-axis and *ab*-plane have been studied in details.

## 2. Experimental details

Single crystal of $La_{0.7}Ca_{0.3}MnO_3$ was prepared by a floating zone technique using radiative heating. The bulk material for crystal growth with the same nominal composition was prepared by using the standard solid state reaction route. The single crystal in the form of a rod was grown. The growth direction of the crystal is close to the [110] axis. $La_2O_3$, $CaCO_3$, $SrCO_3$ and $MnCO_3$ (99.9% purity, *Sigma-Aldrich*) were used as starting materials. $MnCO_3$ was

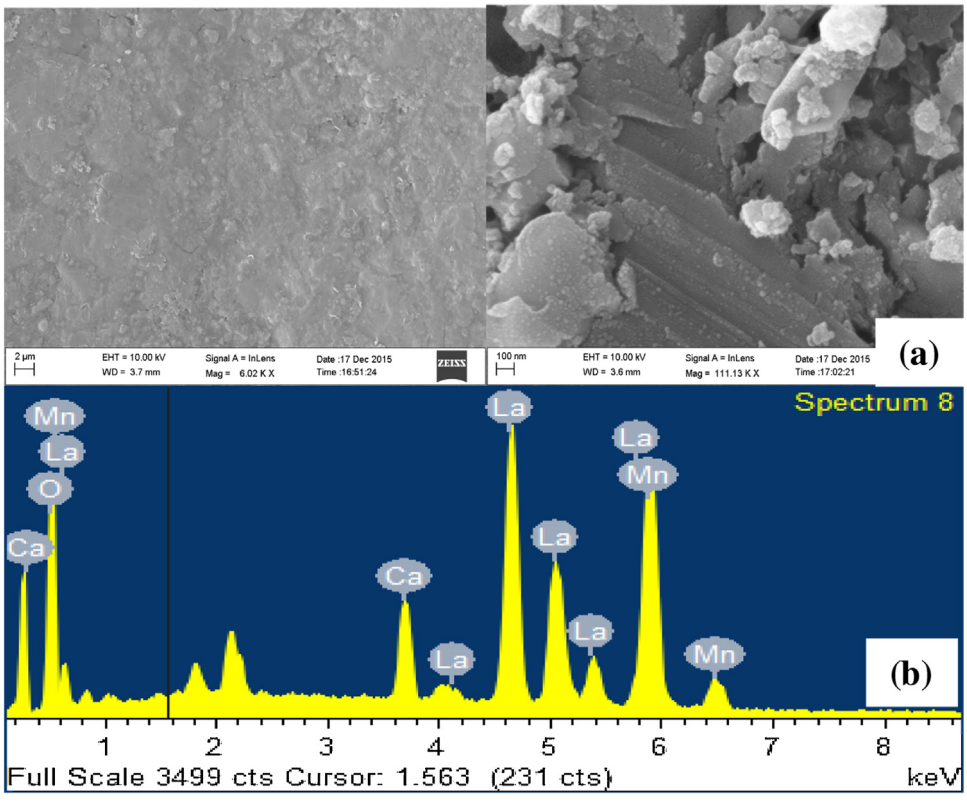


**Fig. 1.** (a) SEM micrograph (b) EDX spectrum for single crystal of $La_{0.7}Ca_{0.3}MnO_3$ (LCMO).