

ABANT İZZET BAYSAL UNIVERSITY
THE GRADUATE SCHOOL OF NATURAL AND APPLIED
SCIENCES



EFFECT OF CATIONIC AND ANIONIC DOPINGS ON
STRUCTURAL AND MAGNETO-TRANSPORT PROPERTIES
OF MANGANITES

DOCTOR OF PHILOSOPHY

SEVGİ POLAT ALTINTAŞ

BOLU, JULY 2015

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APPROVAL OF THE THESIS

Effect of cationic and anionic dopings on structural and magneto-transport properties of manganites submitted by **Sevgi Polat Altıntaş** in partial fulfillment of the requirements for the degree of Doctor of Philosophy in **Department of Physics, Abant Izzet Baysal University** by,

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DECLARATION

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Sevgi POLAT ALTINTAŞ



ABSTRACT

EFFECT OF CATIONIC AND ANIONIC DOPINGS ON STRUCTURAL AND MAGNETO-TRANSPORT PROPERTIES OF MANGANITES

PHD THESIS

SEVGİ POLAT ALTINTAŞ

ABANT İZZET BAYSAL UNIVERSITY GRADUATE SCHOOL OF
NATURAL AND APPLIED SCIENCES

DEPARTMENT OF PHYSICS

(SUPERVISOR: PROF. DR. CABİR TERZİOĞLU)

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Colossal magnetoresistance (CMR) which is defined as the change in resistivity (as much as 1000%) under applied magnetic fields has been a subject of intense theoretical and experimental research since 1990s. The common and the most substantial characteristic of the magnetoresistive materials is that their electrical resistance can be changed significantly by application of an external magnetic field. The most relevant materials showing CMR effect are the compounds that crystallize in the perovskite structure (rare earth-alkaline earth-manganese based $R_{1-x}A_xMnO_{3\pm\delta}$ (RAMO; Re: rare earth metal, Ae:divalent alkaline metal)). Due to their fascinating magnetic and electronic properties, rare earth manganites have a variety of potential applications such as magnetic storage cells for magnetoresistive random access memories, low and high field magnetic sensors and infrared bolometers. This thesis on hole-doped RAMO system has two-fold purpose. One is the investigation of the anion substituted polycrystalline bulk system of $La_{0.7}Ca_{0.3}MnO_{3-\delta}F_x$ ($x=0.0, 0.2, 0.4$ and 0.6). The second purpose is to understand the effect of deficiency/efficiency in the A (=Ca)-site. This class of transition metal oxide under investigation are hole-doped system with $La_{0.7}Ca_xMnO_{3-\delta}F_{2x}$ ($x=0.2, 0.3$ and 0.4). The main objective is the characterization of the structural and physical property and to understand the magneto-transport behavior in these systems. To accomplish this objective, we prepared the samples by solid state reaction method and investigate by means of X-ray powder diffraction, scanning electron microscopy, electrical resistivity and magnetization measurements.

KEYWORDS: Manganites, Magnetoresistance (MR), Metal-Insulator Transition, Deficiency, Efficiency, Curie Temperature

ÖZET

**MANGANİTLERİN YAPISAL VE MANYETO-TAŞINIM ÖZELLİKLERİ
ÜZERİNE KATYONİK
VE ANYONİK KATKILAMANIN ETKİSİ
DOKTORA TEZİ
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FİZİK ANABİLİM DALI
(TEZ DANIŞMANI: PROF. DR. CABİR TERZİOĞLU)**

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Manyetik alan altında % 1000' den büyük direnç değişimi anlamına gelen devasa manyetodirenç (DMD) (colossal magnetoresistance, CMR) 1990'larda ortaya çıkan ilk uygulamalarından beri gerek temel bilimsel kaynağının anlaşılması gerekse teknolojik uygulamalarının geliştirilmesi bağlamında birçok çalışmanın konusu olmuştur. Manyetodirenç özellik gösteren malzemelerin en belirgin ve önemli karakteristiği elektriksel dirençlerinin dışarıdan uygulanan manyetik alanla dikkat çekici ölçüde değiştirilebilmesidir. DMD etkisinin en bariz gözlemlendiği malzeme ailelerinden biri perovskit yapıda kristalleşen nadir toprak elementi-toprak alkali-manganez içeren $R_{1-x}A_xMnO_{3\pm\delta}$ (RAMO; Re: nadir toprak elementi, Ae: iki değerlikli toprak alkali katyonu) genel formüllü bileşiklerdir. Bu malzemeler sahip oldukları olağandışı manyetik, elektronik ve optik özellikleri dolayısı ile manyetik bilgi kaynakları için okuma kafaları, düşük ve yüksek alan manyetik sensörler, kızılötesi bolometreler gibi teknolojik uygulamalarda sıklıkla kullanılmaktadırlar. Boşluk-katkılı RAMO sistemler üzerine olan bu tezin iki yönlü amacı vardır. İlk amacımız anyon-katkılanmış bulk polikristal sistemin, $La_{0.7}Ca_{0.3}MnO_{3-\delta}F_x$ ($x=0.0, 0.2, 0.4$ and 0.6), incelenmesidir. İkinci amacımız A (=Ca)-tarafındaki eksiklik/fazlalık etkisinin anlaşılmasıdır. Bu geçiş-metal oksit sınıfındaki boşluk-katkılı sistem $La_{0.7}Ca_xMnO_{3-\delta}F_{2x}$ ($x=0.2, 0.3$ and 0.4) dir. Ana hedef bu sistemlerdeki yapısal ve fiziksel özelliklerin karakterize edilmesi ve manyeto-tasınım davranışının anlaşılmasıdır. Bu hedefi gerçekleştirmek için gerekli malzemeler katıhal tepkime yöntemiyle hazırlandı ve hazırlanan malzemeler toz x-ışını kırınım, taramalı elektron mikroskopi, elektriksel direnç ve manyetizasyon ölçümleriyle incelendi.

ANAHTAR KELİMELELER: Manganitler, Manyetodirenç (MR), Metal-Yalıtkan Geçiş, Eksiklik, Fazlalık, Curie Sıcaklığı

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LIST OF ABBREVIATIONS AND SYMBOLS

AFI	: Antiferromagnetic insulators
AFM	: Antiferromagnetic
AMR	: Anisotropic magnetoresistance
Au	: Arbitrary unit
CMR	: Colossal magnetoresistance
CO	: Charge ordering
DTA	: Differential thermal analysis
FC	: Field-cooled
FM	: Ferromagnetism
GMR	: Giant magnetoresistance
H_c	: Critical magnetic field
HS	: High spin
K	: Kelvin
LBMO	: La _{1-x} Ba _x MnO ₃
LCMO	: La _{1-x} Ca _x MnO ₃
LSMO	: La _{1-x} Sr _x MnO ₃
MR	: Magnetoresistance
Oe	: Oersted
OO	: Orbital ordering
PM	: Paramagnetic
TGA	: Thermogravimetric analysis
T_C	: Curie temperature
TCR	: Temperature coefficient resistance
T_{MI}	: Metal-insulator temperature
TMR	: Tunneling magnetoresistance
T_N	: Néel temperature
SEM	: Scanning electron microscope
XRD	: X-ray diffraction
ZFC	: Zero Field Cooled

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1. INTRODUCTION

1.1 Overview

Perovskite-structured manganese oxide $R_{1-x}A_x\text{MnO}_3$ (where R is a lanthanide rare earth element and A is a divalent alkaline earth metal ion) compounds have been an intensive subject in material science, primarily because of their complex magneto-electrical and colossal magnetoresistance (CMR) properties (Bingham et al., 2012; Nasri et al., 2013). These interesting magneto-transport properties can be changed by weak disturbances such as chemical doping, applied magnetic field, pressure, temperature, etc., such that these materials reveal technological prospects in magnetic memory storage, faster read-write and sensor devices (Lau & Leung, 2008; Doroftei et al., 2013; Yuan et al., 2007; Gutiérrez et al., 2008). It is generally accepted that the physical properties of the hole-doped mixed valence manganites are governed by the close interaction among charge, spin, lattice and orbital degrees of freedom and nanoscale inhomogenities among competing phases (Zener, 1951, Tokura, 2000; Dagotto, 2002). At present, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO) system is a well-studied manganite system among the large number of pure CMR materials. Substitution of La^{3+} by Ca^{2+} ions improves an average manganese valence to protect the whole electrical neutrality and produces the valence state of Mn ($\text{Mn}^{3+}/\text{Mn}^{4+}$) with the electronic configuration $t_3^{2g}e_1^g$ for Mn^{3+} and t_3^{2g} for Mn^{4+} . Thus, any perturbations on the valence of Mn ions lead the system to engineer from insulating to metallic and paramagnetic to ferromagnetic states (Levy et al., 2002; Millis et al., 1995). In an optimized carrier concentration ($x \sim 0.3$), this system undergoes a paramagnetic to ferromagnetic phase transition at about 250 K which coincides with the insulator to metal transition (Millis, 1998). The most effective way to change the physical properties of the LCMO compounds is either substituting cations at La- or Mn-sites or changing the oxygen content in the ideal cubic perovskite structure. Lots of studies have have been carried out by replacing part of lanthanum by some monovalent (Na, K, Ag, etc.) (Varshney et al., 2010; Mazaheri & Akhavan, 2010; Yadav & Shelke, 2013; Srinivasan et al., 2001) divalent (Sr, Ba, Pb, etc.) (Lim et al,

2009; Salamon & Chun, 2003), or trivalent (Eu, Y, Bi, etc.) atoms (Altintas et al., 2011, 2012, 2013; Zhang et al., 2005; Lalitha & Reddy, 2010). This procedure showed fascinating evolution of the magnetoelectrical transport properties of these compounds. Furthermore, so many reports on the substitution of 3d transitional metals such as Cr, Ni or Co at Mn site have been analyzed deeply by many groups (Kumar et al., 2010, Orlova et al., 2009; Nisha et al., 2013; Li et al., 2007). However, a review of the literature shows that the role of anion substitution on the physical properties of the hole doped manganites has been studied poorly (Guo et al., 1999, 2000a, 2000b; Kreutzbruck et al., 2007]. Several studies have shown that the fluorine atom has played an intriguing role in many high-temperature superconductors and its substitution reduces the hole concentration and affects the superconducting properties (Hamdan & Hussain, 2009; Amira et al., 2004, 2005; Amirouche et al., 2013). Also, the oxygen content of manganites is an important factor that can strongly effect their physical properties. Since oxygen is at the center of the Mn-O-Mn bond, its nonstoichiometry can greatly affect the valence states, local lattice distortions as well as the orbital order (Zhao et al., 1999).

The main aim of this thesis is the systematic investigation of the anionic and cationic doping at A- and O-site of manganite systems. By such a doping, we plan to improve/optimize magnetoresistive properties. The studied material system $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ as a member of the class of mixed-valence manganites offers a large variety of structural, magnetic and transport properties. In order to examine the effect of A- and O-site substitution, we have prepared two series of high quality bulk samples by the solid state reaction method. The investigated materials are: $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_{2x}$ with $x = 0.0, 0.2, 0.4$ and 0.6 and $\text{La}_{0.7}\text{Ca}_x\text{MnO}_{3-\delta}\text{F}_{2x}$ with $x=0.2, 0.3$ and 0.4 . We have performed X-ray powder diffraction, electrical resistivity and magnetization measurements to characterize the produced samples.

The thesis has been divided into six chapters:

Chapter 1 is the overview of the thesis; the content of the each individual chapter is briefly summarized here. A brief history of the manganites has been given along with their importance for the scientific community. This chapter also involves the basic theory of manganites and their most important properties.

In Chapter 2 we described our experimental set up and measurement methods. All the experimental characterization techniques used are briefly discussed in the specific sections.

The main results of this research, consisting of the electric and magnetic transport measurements down to around 5 K, are presented in chapter 3.

In Chapter 4 the theoretical aspects are presented. Models and approximations are discussed in detail, and results are analyzed. Especially, the key importance of the recently found phase separation scenario is discussed.

Chapter 5 is devoted to investigate the studies on the structural, electric and magnetic transport properties of A-site non-stoichiometric LCMO samples. The electrical conduction mechanism in the entire temperature range is explained by a simple phenomenological model that the system consists of the phase-separated FM and PI regions.

Chapter 6 is a general summary of all chapters and we have shown some highlights of important results that obtained during this thesis.

1.2 History

The interest for the CMR-materials starts with the 1950 papers by Jonker and Van Santen (Jonker & Van Santen, 1950; Van Santen & Jonker, 1950). They crystallized the first mixed-valence manganites of $\text{LaMnO}_3\text{-CaMnO}_3$, $\text{LaMnO}_3\text{-SrMnO}_3$ and $\text{LaMnO}_3\text{-BaMnO}_3$. They found that the end members of the series, corresponding to $x = 0$ and $x = 1$, were antiferromagnetic insulators (AFI). However, intermediate values of 'x' gave ferro-magnetism (FM), particularly around $x = 0.30$. It was observed that the onset of ferromagnetism was associated with a sharp increase in electrical conductivity. Later theoretical works tried to explain these unusual phenomena and Zener's paper is probably the most important ones. His paper deals with the interaction between electrons in the d-shells in ferromagnetic manganites (Zener, 1951). This is the paper where the idea of double exchange, which is believed to be the principal mechanism in these materials, was introduced. Volger (1954) reported the occurrence of magnetoresistance (MR) in these materials. In order to evaluate the magnetic phase profile in these materials, Wollan and Koehler (1955) carried out extensive neutron diffraction studies on $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. The study of Wollan and Koehler clearly established the presence of ferromagnetic (FM) and antiferromagnetic (AFM) regions and occasionally the simultaneous occurrence FM and AF regions in LCMO system. Goodenough and Longo (1970)

followed up this paper with theoretical predictions for the origin of the magnetic ordering, and additionally, predicted an orbital and charge ordered state. Von Helmholt et al. (1993) described the magnetoresistance in $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$, which was about 60%, and the interest really took off with the papers by McCormack et al. (1994). In the same year, Jin and his group found the magnitude of magnetoresistance that exceeded 99.92%¹ (Jin et al., 1994). This huge magnetoresistance observed at 77 K for a film made of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$, and the effect was named colossal magnetoresistance. A detailed review about metal-insulator transitions was published by Imada et al. (1998), followed by Coey et al. (1999) who studied deeply various parts of manganite physics, such as analyzing electronic ground states, the extrinsic effects like pressure and temperature, the electronic transport behavior. Dagotta and his group (2001) published an extensive report about the phase separation in CMR and this report includes a deep understanding of CMR systems. At the beginning of the millennium, many regarded the manganites as well understood systems (Salamon & Jaime, 2001; Edwards, 2002).

Since 1994 when the CMR-term was coined there have been more than 4600 papers published about this effect². Apart from the huge MR, manganites exhibit a very rich composition-temperature (x-T) phase diagram which makes them more fascinating. Depending upon the size of the A-site cations, most of interesting phenomena such as paramagnetic-ferromagnetic (PM-FM) transition at Curie temperature (T_C), metal-insulator transition, MI, at temperature T_{MI} , CMR, antiferromagnetism (AFM) at Néel temperature (T_N), charge ordering/orbital ordering (CO/OO) at T_{CO} , etc. are observed (Ramirez, 1997; Tokura, 2006; Siwach et al., 2008; Rao & Raveau, 1998; Coey et al., 1999; Tokura, 2000).

After the discovery of the CMR effect, there was an enormous work trying to make CMR materials for practical use in magnetic sensors. The success of the giant magnetoresistance in multilayers has triggered this interest. However, it has been

¹In their report they used the definition of MR as $\Delta\rho/\rho(H)$ which gives a value of 127000%.

²Search for “colossal magnetoresistance” on Science Citation Index Expanded done on May 31, 2015.

found that it will be very difficult, or even impossible, to make the CMR effect useful, the problem being that, the level of magnetoresistivity required for practical devices can be achieved only under very high fields for this class of materials. Also in the view of the underlying physics of CMR materials, till now a clear and unified explanation has not been given yet. One of the best descriptions recently proposed is based on electronic phase separation scenerio. This scenerio includes the coexistence of at least two different magnetic/electronic phases, such as paramagnetic insulator and ferromagnetic metallic. Their interaction and percolation determines the basic properties of the compound (Becker et al., 2002; Fäth et al., 1999; Uehara et al., 1999; Renner et al., 2002; Yunoki et al., 1998).

1.3 Characteristics of Perovskite Manganites

Mixed-valence manganites form a class of oxide materials, which diversity in their large variance in properties (Salamon & Jaime, 2001). Generally, these materials form a distorted perovskite structure ABO_3 , where Mn is positioned on B-site and the A-site is shared by trivalent rare earth cations (R) such as La, Ce, Pr or Nd and divalent alkaline earth cations (A) like Ca, Sr or Ba. The composition $R_{1-x}A_xMnO_3$ can be regarded as a solid solution of $RMnO_3$ and $AMnO_3$, while A^{2+} acts as acceptor dopant for the $RMnO_3$ host crystal due to the formal charges $((R_{1-x}^{3+}A_x^{2+})(Mn_{1-x}^{3+}Mn_x^{4+})O_3^{2-})$. Depending on the cation species, stoichiometry and temperature, these oxides exhibit different structural, magnetic and transport properties. The nominal electronic configurations of the Mn^{+3} and Mn^{+4} are $3d^4$ and $3d^3$, respectively.

1.3.1 Crystallographic and Electronic Structure

Perovskites are oxides that have ABO_3 structure, where large cations such as rare earth (La, Sm, Nd, Pr, Dy) and alkaline earth (Sr, Ca, Ba, Pb) ions occupy the A-site and smaller cations like 3d transitions metal ions (Mn) occupy the B-site. The compounds where the B-site is occupied by Mn ions are called. The geometric structure can be represented using a cubic unit cell with A-site ions occupying the

corners (0, 0, 0) and B-ions occupying the body centre ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). The oxygen ions occupy the face center ($\frac{1}{2}, \frac{1}{2}, 0$) as in Figure 1.1 forming an octahedron around the B ions. Crystal structure depends on the composition. The A, B and O atoms are in 12, 6 and 6 coordination respectively.

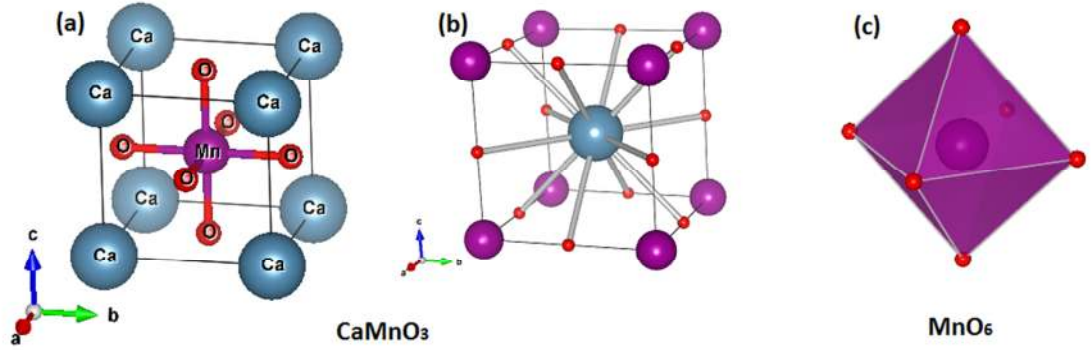


Figure 1.1. (a)-(b) Model for the perovskite manganite of CaMnO_3 , (c) MnO_6 octahedra.

In Figure 1.1, a typical perovskite structure is shown. Using La and Ca as A site atoms and Mn as the B site atom, the A site atoms, especially La atoms, are larger than the Mn atoms in the B site. This means that the A site atoms dominate the overall crystalline structure. Considering perovskite structure consisting of more A site atoms than B site, the larger A site atoms will expand the crystalline structure in the direction of the La atoms, which will deform and strain the structure creating a non-cubic or non-ideal structure.

The structure of this compound can be characterized by the Goldschmidt tolerance factor t , where;

$$t = \frac{r_A + r_O}{\sqrt{2}r_B + r_O} \quad (1.1)$$

R_A , R_B and R_O are the ionic radii of rare earth, Mn ions and oxygen, respectively. Tolerance factor is a measure of the stability and degree of distortion of a structure. It also measures the deviation from perfect cubic structure ($t = 1$) (Ramirez, 1997). Structures with $0.8 \leq t \leq 0.9$ are orthorhombic, those with $0.9 \leq t \leq 0.97$ are cubic, and those with $0.97 \leq t \leq 1.02$ have tetragonal structure (Hezareh, 2005).

The basic material of the lanthanum manganite family is LaMnO_3 and it has an orthorhombic structure with $t=0.89$. From the conditions, a very slight increase in t induced by substituting larger ions like Ba^{2+} or Sr^{2+} for La^{3+} is needed for transition to a cubic structure (See Table 1.1). In this thesis, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO) is considered as the reference materials. Substituting Ca^{2+} for La^{3+} ions reduces the average value of r_B and consequently increases the tolerance factor to a value above 0.96 which would lead to a rhombohedral perovskite structure. This kind of substitution causes a decrease in the volume of the unit cell which creates distortions in the structure. These distortions lead to change the electronic and magnetic properties in the system (Jonker & Van Santen, 1950).

Table 1.1. Ionic radii in Ca-, Sr- and Ba-doped lanthanum manganite perovskites. The A- site cation radii are given for twelve-fold and nine-fold coordination number (separated by comma), while the B-site cation radii are given for six-fold coordination number. Source: Shannon (1976).

	A-site (Å)	B-Site (Å)	O-site (Å)
La^{3+}	1.36, 1.216	$\text{Mn}^{4+} \rightarrow 0.53$	$\text{O}^{2-} \rightarrow 1.4$
Ca^{2+}	1.34, 1.18	$\text{Mn}^{3+} \rightarrow 0.64$	-
Sr^{2+}	1.44, 1.31	$\text{Mn}^{3+} \rightarrow 0.64$	-
Ba^{2+}	1.61, 1.47	$\text{Mn}^{3+} \rightarrow 0.64$	-
F^-	-	-	1.33

1.3.2 $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$

In this subsection, the magnetic phase diagram of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ will be analyzed. Since to understand the structural, electronic and magnetic properties, we need to introduce the phase diagram of lanthanide manganites. This compound presents some characteristics of large bandwidth manganites, such as the presence of a robust ferromagnetic metallic phase. However, it also has features that indicate strong deviations from double-exchange behavior, including the existence of charge/orbital-ordered phases. For this reason, the manganite community considers that this compound should be labeled as of “intermediate bandwidth”, to distinguish it from the truly low-bandwidth compound $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ where a metallic ferromagnetic phase can only be stabilized by the application of magnetic fields.

In fact, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ is a well analyzed system since the early days of manganite studies (Jonker & Van Santen, 1950; Wollan and Koehler, 1955; Matsumoto, 1970). However, after the discovery of the CMR effect observed in hole-doped lanthanum manganites, there has been a revived interest in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ system. The drop in resistivity, ρ , with decreasing temperature and the peak in magnetoresistance are correlated with the ferromagnetic transition in the magnetization (Dagotto, 2001). The insulating behavior above the Curie temperature is very eminent and the explanation of its origin is among the most important issues to be figured out in theories of manganites. Below T_C the presence of ferromagnetism was tentatively attributed to the double-exchange mechanism. However, soon after the initial reports, it was pointed out by Millis and coworkers (1995) that Zener's double exchange model was incapable of explaining the large magnetoresistance effect observed. Therefore, in addition to the double exchange, lattice distortions of Jahn-Teller type (Jahn and Teller, 1937) were discussed.

The complete phase diagram in dependence on temperature and doping level x for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ system can be found in Fig. 1.2. It should be noted that the phase diagram is based on magnetization and resistivity measurements and taken from Cheong and Hwang (1999). One can clearly see from the diagram that the FM phase absolutely occupies just a fraction of the whole diagram, illustrating once again that DE does not provide a full understanding of the manganites. For example, equally prominent are the charge ordered (CO) states between $x = 0.50$ and 0.87 . The CO state at $x = 0.50$ was already described by Wollan and Koehler (1955) as a CE-state. "In the regime of CO-states, studies by Ramirez et al. (1996) of the sound velocity, specific heat, and electron diffraction were attributed to strong electron-phonon coupling, in agreement with the predictions of Millis et al. (1995)" (Dagotto, 2001). The end members are both antiferromagnetic (AF) and insulating. At around x close to 1, the system shows a mixed-phase state with coexisting FM-AF characteristics based on recent theoretical calculations (Dagotto, 2002). In the low doping regime, the system shows a charge-ordered phase, and a curious ferromagnetic insulator. Ibarra and De Teresa (1998) showed that at $x = 0.10$, there is no large magnetoresistance effect using fields of 12 T. Also, it has been shown that at $x=0.65$, well inside the charge-ordered state, a 12 T field is also not sufficient to destabilize the insulating state into a metallic one. For this reason, in order to get

large magnetoresistance effect, the doping regime must be closer to that leading to the FM metallic regime. In Fig. 1.2, let me analyze a well-defined feature where the minimum resistivity and the best ferromagnetism (highest Curie temperature) coincide for $x \approx 0.3$. In the region of interest for this thesis, $x \approx 1/3$, the Curie temperature is $T_C \approx 260\text{K}$ which coincide with metal-insulator transition temperature. The value of $x = 1/2$ is the boundary between the FMM phase and the AF and CO (insulating) phase persisting until $x = 7/8$, with maximum T_{CO} at $x = 5/8$.

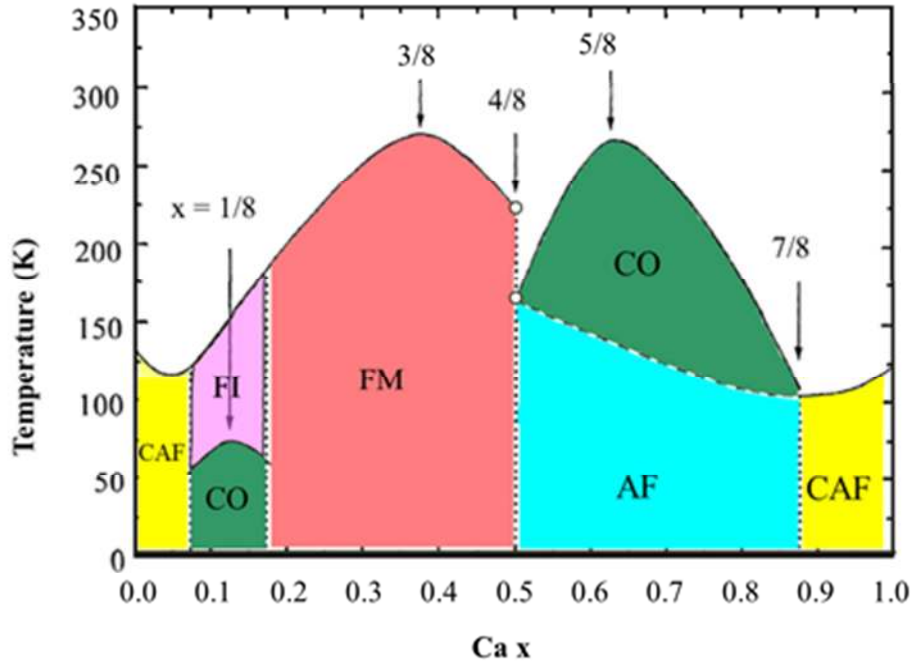


Figure 1.2. Phase diagram of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, constructed from measurements of macroscopic quantities such as the resistivity and magnetic susceptibility, reproduced from Cheong and Hwang (1999) edited by Tokura (2000). FM: Ferromagnetic Metal, FI: Ferromagnetic Insulator, AF: Antiferromagnetism, CAF: Canted AF, and CO: Charge/Orbital Ordering. FI and/or CAF could be spatially inhomogeneous states with FM and AF coexistence.

The FM state is optimal (maximum T_C) for doping $x = 3/8$, and also $x = 5/8$ seems to be the highest T_C for the CO state in manganites. It is important to realize that within a simple one-orbital double-exchange model, the optimal density for ferromagnetism should be $x=0.50$. The fact that this is not observed is already indicative of the problems faced by a double-exchange description of manganites. These anomalies at commensurate concentrations show once more the importance of the electron-lattice coupling in the manganite perovskites (Coey et al., 1999). Given

the strong interconnection between structure, magnetic and transport properties, one may expect that external distortions like strain induced from a substrate in thin films, may also lead to change these properties (Carbone, 2004).

1.4 Important interactions in Manganites

1.4.1 Double Exchange Mechanism

The most important theoretical explanation to the microscopic physics of the manganites was given in a series of papers by Zener (1951a, 1951b, 1951c). He demonstrated that the existing magnetic exchange models failed to explain the situation in manganites and presented what is now known as the ‘double exchange’. We can simply define the double exchange as an interaction that occurs between two unequal $\text{Mn}^{3+}/\text{Mn}^{4+}$ ions in mixed-valent perovskites through an oxygen atom. It is crucial for the FM and metallic properties of the manganese oxides (Von Helmolt et al., 1993). Anderson and Hasegawa (1955) have formalized the DE mechanism through a formalized semi-classical model. Zener has proved the DE mechanism and the states of manganites are assumed to be uniform. According to his theory of the indirect magnetic exchange between 3d atoms, FM interactions are favored when the magnetic atoms are fairly well separated, leading to active conduction electrons. Starting from the insulating AFM LaMnO_3 to end member where electrons are localized on the atomic orbitals, Zener (1951b) showed how the system should gradually become more FM upon hole-doping (introduction of Mn^{4+} by doping of divalent atom like Ca^{2+}). In addition, the problem of the exchange between Mn^{3+} and Mn^{4+} ions by an oxygen ion was accounted and then the concept of simultaneous exchange of an electron from the Mn^{3+} to the oxygen and from the oxygen to the neighboring Mn^{4+} is inserted, as shown in a simple sketch in Figure 1.2. With two neighboring Mn sites, the single e_g electron present on one of the d^4 sites can be transferred to the opposite Mn site by way of a spin-preserving transfer via the oxygen ion. The valence electron of oxygen on the site connecting to two manganese atoms, with the same spin as the e_g , transfers to the d^3 Mn site at the same time as an e_g moves from the d^4 to the vacancy on the oxygen (Zener, 1951b, 1951c).

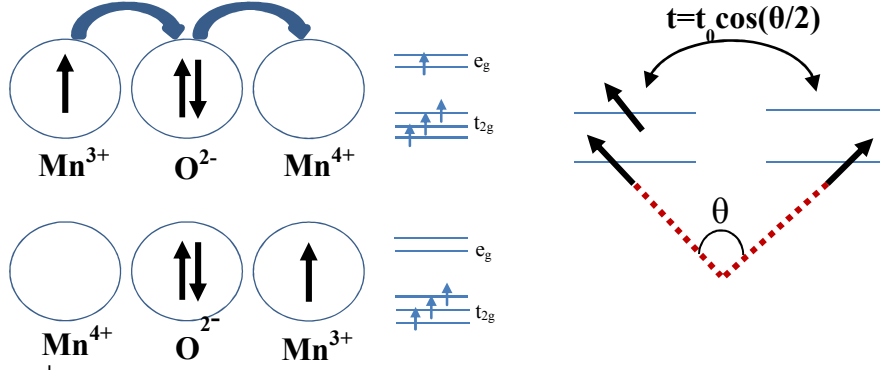


Figure 1.3. A schematic diagram of the double exchange mechanism proposed by Zener and (right) relative configurations of the spin-canted states (left).

It should also be noted that all individual ion or atom is enforced by a ferromagnetic Hund (Hund's rule) coupling J_H . The conduction electrons do not change their spin as they progress from ion to ion. These electrons are able to move in the crystal in a hopping manner when the net spins of the incomplete d shells are parallel, that is the conduction electrons lower their kinetic energy if the background of d shell spins or the t_{2g} spins of manganite is fully polarized.

The existence of metal-insulator transition behavior of $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ mixed-valent manganites is explained in the framework of DE interaction which arises as a result of a strong exchange interaction between the itinerant e_g electrons (or holes) and localized t_{2g} spins through the Mn-O-Mn path. The effective hopping (t_{eff}) of an electron between two nearest neighbor Mn ions has been studied extensively by Rodriguez et al. (2000). Their formalism have showed that $t_{\text{eff}} = t \cos \theta / 2$, where θ is the angle between t_{2g} spins located at the two Mn sites involved in the electron transfer. The tilting and twisting of the oxygen octahedral have been observed due to the ionic mismatch between La and A ions. Tilting of the octahedral can be measured with the distortion of the Mn-O-Mn bond angle and bond length (Rodriguez et al., 2000).

The spins S_1 and S_2 of the two ions are coupled by exchange interactions and Hamiltonian (H) as,

$$H_{ex} = \sum_{i,j} J_{ij} S_i S_j \quad (1.2)$$

where J is the exchange integral and S is for the electron spin. When J is less than zero, it reveals the FM coupling stabilizing an $S = 9/2$ ground state. On the other hand, J is greater than zero for AFM with $S = 1/2$ ground state. In general, AFM coupling dominates, leading to anti-parallel alignment of the spins. According to this proposed mechanism, the translocation of an electron takes place from one Mn to another through an overriding O^{2-} ion. The translocation takes place in two steps due to doubly occupation of oxygen in p orbitals. The movement of an electron takes place from oxygen to the left Mn followed by a transfer of a second electron from the right Mn into the vacated oxygen orbital and hence, known as DE. In addition, another H is developed due to cluster spin and is reported as,

$$H = J S(S + 1)/2 \pm B(S + 1/2) \quad (1.3)$$

where B is the strength of the DE interaction (Papaefthymiou et al. 1987).

1.4.2 Jahn-Teller (JT) Distortion

Jahn and Teller (1937) was proposed a theorem which explains some of the distortions observed in transition metal complexes. It states that “any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy” (Jahn & Teller, 1937). This distortion is called JT distortion or JT effect. 3d energy levels of cations of transition metal complexes surrounded by oxygens creating octahedron are split by the crystal field (crystal-field splitting is responsible for lifting the degeneracy of the 5-fold degenerate d-states, but leaves a two e_g -state set with equal energies) into two levels: double degenerated e_g level and triple degenerated t_{2g} level. When the lattice has predominantly Mn^{3+} ions then one can observe a cooperative static JT-effect with a permanent distortion of the lattice structure. While, for Mn^{4+} there are no static JT-distortions because the e_g -shells are empty. When a Mn^{4+} ions is replaced locally by a Mn^{3+} then there is one additional electron at the e_g -orbit of one lattice site. For example, in LCMO system, the Mn^{3+} ion has a d^4 configuration. In octahedral symmetry, the d level splits into three t_{2g} and two e_g orbitals. The Mn^{3+} ion has high-spin configuration, with three electrons occupying the three t_{2g} orbitals and one electron occupying the doubly degenerate e_g

orbitals as $t_{2g}^3 e_g^1$. According to the JT theorem, the structure will distort thereby removing the degeneracy of the e_g orbitals. In solids, the orbital degree of freedom of the Mn^{3+} ion often shows long-range ordering associated with the co-operative JT effect. It is observed for the most extensively studied compounds throughout the LCMO series, that is $LaMnO_3$, that below a transition temperature T_{JT} , the $3d_{3x^2-r^2}$ and $3d_{3y^2-r^2}$ orbitals are ordered in the ab plane in an alternating manner.

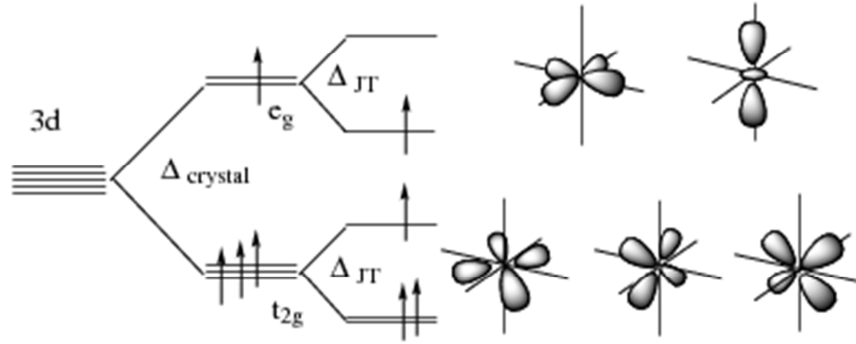


Figure 1.4. Two e_g and three t_{2g} energy levels and orbitals of Mn^{4+} and Mn^{3+} in a crystal field of octahedral symmetry. The splitting of e_g and t_{2g} energy levels due to Jahn-Teller distortion is also shown (taken from Tokura and Tomioka, 1999).

In manganites, the orbital degeneracy of the e_g electrons are lifted because of the movement oxygen ions from their original positions. There are 21 modes of vibration for the movement of oxygen and Mn ions (Orbach and Stapleton, 1972). However, only two modes of vibrations are responsible for the splitting of the e_g doublet. These are two types of distortions (Q_2 and Q_3) associated with the JT effect (Tomioka et al., 2001). The Q_3 is a tetragonal distortion that results in an elongation or contraction of the MnO_6 octahedron corresponding to the filled $3d_{3z^2-r^2}$ or $3d_{x^2-y^2}$ orbital. The Q_2 is an orthorhombic distortion obtained by a certain superposition of the $3d_{3z^2-r^2}$ and $3d_{x^2-y^2}$ orbitals (Kanamori, 1960) (See Fig. 1.5). The oxygen framework is described in Pbnm space group symmetry by two oxygen (O_1 and O_2) positions. The O_1 position is situated on the mirror plane and is attributed to the out-of plane oxygens; the O_2 position is attributed to the inplane oxygens. The rotations of the octahedra are reflected in the deviation from 180° of the Mn-O-Mn tilting angle. The JT effect in $LaMnO_3$ is dominated by the Q_2 distortion with alternating long (l) and short (s) Mn-O₂ bond lengths in the ab plane and a

medium out-of-plane Mn-O₁ (m) bond length. The medium bond length (m) deviates from the average bond length, such that $m < (l + s)/2$ indicates that the JT distortion is not of a pure Q₂ type. A contribution of the Q₃ distortion is also present in these oxides.

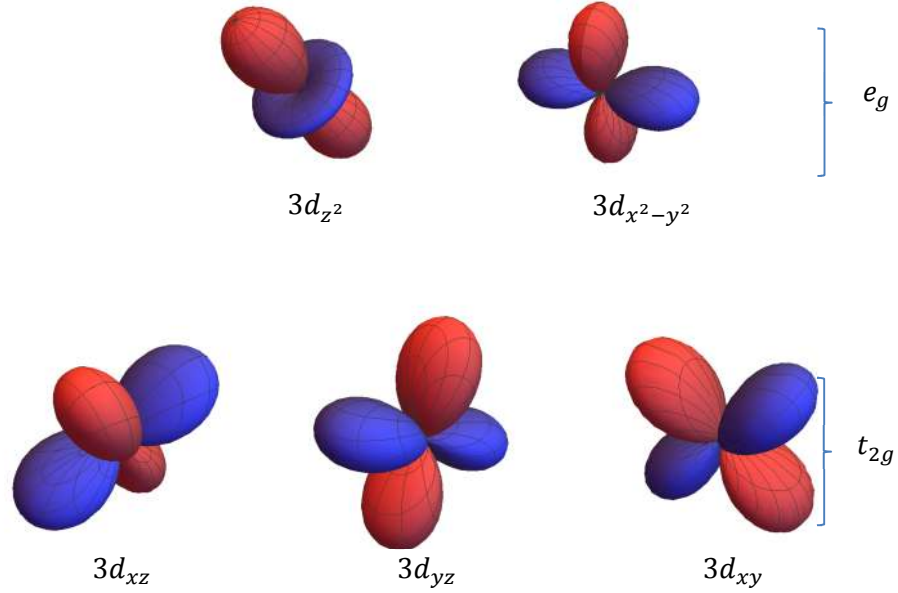


Figure 1.5. Angular wave functions of the e_g and t_{2g} orbitals.

1.4.3 Charge and Orbital Ordering

We can define charge ordering as the ordering of the metal ions in different oxidation states in specific lattice sites of a mixed-valent material. In such ordering, the electrons in the material generally localized which makes the material insulating or semiconducting because when the charges are localized, electrons cannot easily hop from one cation site to another. This phenomenon was first proposed by Eugene Wigner (1930). In LCMO system, at certain values of cation doping, $x=0.5$, the CE-type charge ordered state is observed at low temperature. This state is thought to comprise spatial segregation of Mn^{4+} and Mn^{3+} ions. At doping concentrations being rational fractions the mobile electrons (or holes) can be localized on certain manganese ions forming a regular lattice of Mn^{3+}/Mn^{4+} (known as Wigner

crystallization). The state is also thought to be orbitally ordered, with the e_g electron occupying $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ orbitals on alternate sites, and to have anti-ferromagnetic spin ordering (Goodenough, 1955; Radaelli et al., 1997). Ordering of the Mn^{3+} and Mn^{4+} ions produces a $\sqrt{2}a \times \sqrt{2}a$ unit cell, where a is the basic unit cell size. Including the effect of orbital order gives a $2\sqrt{2}a \times \sqrt{2}a$ unit cell. Although strictly the CE-type of order implies spin and orbital order as well as charge order (Goodenough, 1955), it has been frequently used in the literature (Li et al., 1999) to mean just the $\sqrt{2}a \times \sqrt{2}a$ charge ordering, hence the use of ‘CE-AFM’ to denote a state which is also spin ordered. Charge-ordering favors AFM. CO competes with DE, giving rise to interesting properties which are sensitivity to factors like the A-site cation size, the doping level etc. The cooperative J-T effect induces other effects like lattice distortion and also adds to the electron localization in the CO state.

Wollan and Koehler (1955) and later Jirak (1985) carried out a detailed study of the magnetic properties of the $La_{1-x}Ca_xMnO_3$ series including the end members $LaMnO_3$ and $CaMnO_3$ using neutron diffraction in order to determine their magnetic structures. Phases of the composition $LaMnO_3$, $CaMnO_3$, and $La_{0.2}Ca_{0.8}MnO_3$ were found to display antiferromagnetic behavior arising from different magnetic structures, at the same time a narrow composition range around $La_{0.65}Ca_{0.35}MnO_3$ was ferromagnetic. The composition $La_{0.5}Ca_{0.5}MnO_3$ is particularly interesting as mentioned above since these materials give the Mn^{3+} - Mn^{4+} ratio $Mn^{3+}/Mn^{4+} = 1$. This would give equal numbers of J-T active as well as inactive centres. Radaelli et al. (1997) have showed that the structure of Mn-O-Mn bond lengths coherent with the distinct Mn^{3+} and Mn^{4+} sites (by using x-ray scattering techniques).

1.4.4 Indirect Exchange Interaction: Superexchange

Another interaction is antiferromagnetic superexchange (SE) interaction which is first observed by Kramers (1934) and was developed by Anderson and Hasegawa (1950). We can define SE as an indirect exchange interaction between non-neighboring magnetic ions which are mediated by a non-magnetic ion which is placed between them. The distance between the magnetic ions is too large for direct exchange interaction. The SE interaction is a virtual exchange between electrons of

magnetic ions with electrons from the same 2p orbital of oxygen, which have antiparallel spins according to Pauli's exclusion principle (Goodenough, 1955). In the case of MnO or ABO_3 , the $\uparrow$ spin p-electron can hop to the left, cation A, and thus d-spins are either in the parallel $\downarrow\downarrow$ or anti-parallel $\downarrow\uparrow$ configuration. In such a situation the parallel configuration costs more energy and violates the Pauli exclusion principle, thus the effective exchange is antiferromagnetic. Whereas, the geometry of the environment, e.g. 180° bond angle ($\text{M}-\text{O}^{2-}-\text{M}$) generally creates the greatest strength of the anti-parallel coupling between metal ions M, play an important role, and can even decide the sign of the interaction. One another example is LaMnO_3 that contains only Mn^{3+} ions. The LaMnO_3 has an A-type antiferromagnetic structure where ferromagnetic $\text{Mn}^{3+} - \text{O} - \text{Mn}^{3+}$ superexchange dominates within parallel lattice planes and produces a well-defined ordering of the orientation of the occupied e_g orbitals, with neighboring planes coupled antiferromagnetically (Millis et al., 1996a, 1996b).

1.5 Conduction mechanisms in LCMO

1.5.1 High Temperature Region

In the high temperature regime at $T > T_C$, LCMO is usually a paramagnetic insulator (PMI). In this regime, electric conductivity is governed by electrons hopping through a dielectric insulator. There are three major possible mechanisms for conduction in this regime, each supported by some experimental evidence: i) thermally activated hopping model (Kusters et al., 1989) ii) the nearest neighbours hopping model (Snyder et al., 1996) and iii) a variable range hopping (VRH) model (Viret et al., 1997). Since the experimental observations are carried out in a narrow temperature range just above T_C it is sometimes very difficult to distinguish between these three mechanisms. Consequently, there is no agreement as to which mechanism actually prevails.

1.5.1.1 Thermally activated carriers

In this model, the carriers are thermally excited across the band gap from the valence band to a conduction band. The resistivity ρ follows the Boltzmann law, as shown in equation 1.1, where E is the energy gap and ρ_0 is the resistivity at temperature increasing to infinity.

$$\rho = \rho_0 \exp\left(\frac{E}{k_B T}\right) \quad (1.4)$$

This simple model is based on the resistivity given by $\rho = (n e \mu)^{-1}$, where n is the carrier density in the conduction band, e is the charge of an electron and μ is the carrier mobility. The dominant factor is normally the thermally activated form of n , and μ is assumed to be independent of temperature. It would be reasonable for the mobility to show some temperature dependence, which would introduce additional factors into equation 1.4. If the conduction mechanism in the insulating paramagnetic and charge ordered phases is due to thermally activated carriers, then the activation energy should be different for different phases. A transition from the paramagnetic to charge-ordered states would then show up via a sudden change of gradient in the logarithm of resistance versus temperature.

1.5.1.2 Nearest neighbor hopping

In the paramagnetic state e_g electrons are thought to be associated with lattice distortions (i.e. they form polarons). Electrical conduction proceeds via polaron motion. In this model, the lattice distortions are of a size similar to unit cell size and the polarons move between the nearest neighbor sites. The resistivity in this case is given by:

$$\rho = A T \exp\left(\frac{E}{k_B T}\right) \quad (1.5)$$

where A is a constant and E is the energy required to move a polaron.

However, the strong electron-polaron coupling seen in the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ means that the motion of the charge-carriers is slow compared with the lattice

vibration. The motion of the electrons and the lattice cannot be separated, analysis in a non-adiabatic limit is more complicated (Mott, 1993) and the resistivity is given by:

$$\rho = A T^{3/2} \exp\left(-\frac{E}{k_B T}\right) \quad (1.6)$$

1.5.1.3 Variable range hopping

If the activated energies for hopping to neighbouring atoms are not the same, then it may be that hopping to a non-nearest neighbour has a smaller activation energy. This is particularly true at low temperatures (Mott, 1968). This variable range hopping is more complicated to describe (Mott, 1995), but it can be summarized to:

$$\rho = \rho_{\infty} \exp\left(\frac{T_0}{T}\right)^{1/4} \quad (1.7)$$

where T_0 is a characteristic temperature.

One drawback of VRH models is that the values of T_0 are often implausibly high (Loudon, 2003, 2005). Another problem is that VRH was originally proposed for short distance hopping at low temperatures. There is further complication in that, the mechanism may depend on the type of the sample (single crystal, polycrystalline or thin film) (Ziese & Srinitiwara Wong, 1998). The same group reported that the resistance of epitaxial LCMO films showed thermally activated behavior. This discrepancy is probably due to the presence of grain boundaries in the polycrystalline sample (Ziese & Srinitiwara Wong, 1998).

1.5.2 Percolation Region

At temperature $T = T_C$, where T_C is a Curie temperature, PM phase turns into ferromagnetic (FM). In LCMO system the same temperature happens to be also a Metal-Insulation (M-I) transition temperature $T = T_{MI}$, where the insulating phase turns to a metal like one. Therefore, in our sample we have $T = T_C = T_{MI}$ and the PMI

phase observed in high temperature turns into ferromagnetic metallic (FMM) state. The transition leads to a percolation metallic-like conductivity in the FM state. With decreasing temperature, more FM clusters are formed, enhancing percolation paths. The behavior of the resistivity ρ is expected to follow:

$$\rho \propto (p - p_c)^{-t} \quad (1.8)$$

where p is the concentration of the metallic phase, p_c is the critical concentration and t is the critical exponent of the resistivity. In the vicinity of the transition, the metallic concentration is proportional to magnetization, which is approximately a linear function of $(T_C - T)$. Hence, instead of concentration, we can use $(T_C - T)$, which will result equation 1.8 to follow the power law:

$$\rho \propto (T - T_c)^{-t} \quad (1.9)$$

With more temperature decreasing, the intense competition between FMI and FMM phases gives rise to appearance of intrinsic tunnel barriers, interrupting metallic percolating paths. The dominant conduction mechanism crosses over, as a function of barrier thickness (hoping length), from a directed hopping, seen in FM regime, through resonant and direct tunneling, to indirect, inelastic tunneling. Low temperature resistivity is dominated by tunneling across intrinsic barriers (Dolgin, 2010).

1.5.3 Low Temperature Region

In the metallic region the resistivity has been found to be quite well described by;

$$\rho = \rho_0 + B T^2 + C T^n \quad (1.10)$$

where ρ_0 is the residual resistivity at $T = 0$, B is the electron-electron scattering coefficient and C is the electron – phonon or electron – magnon scattering coefficient depending on (Snyder et al., 1996). For example, the value of n has been predicted to be 5 for electron – phonon scattering while it has a value of 4.5 for electron-magnon scattering (Kubo & Ohata, 1972).

1.6 Magneto-Resistance (MR)

Usually the resistivity of a material depends on temperature only. But for some materials the electrical resistivity depends on the value of applied magnetic field. This property is called magneto-resistance. The physical quantity magnetoresistance (MR) is defined as the ratio of change in resistance to the zero field resistance.

$$MR = \frac{R(H)-R(0)}{R(0)} \quad (1.10)$$

where $R(H)$ and $R(0)$ designate resistance in the applied field (H) and zero field respectively. It can be broadly classified into two; Giant Magneto-resistance (GMR) and Colossal Magneto-resistance (CMR). However, there are other types of MR such as tunneling magnetoresistance, anisotropic magnetoresistance, ordinary magnetoresistance, extraordinary magnetoresistance. In the following subsections, we will describe other types of MR shortly.

1.6.1 Tunneling Magnetoresistance

One of the most interesting aspects of spin-dependent tunneling arises when two FM materials separated by a very thin insulator layer which is named as a magnetic tunnel junction (TJ). One of the ferromagnetic layers has a fix magnetic orientation while the other can be changed with an external magnetic field. There are two possible configurations: the antiparallel and the parallel. The carriers can only tunnel from one side to the other in the parallel configuration. Hence, the corresponding resistances are different for parallel and antiparallel magnetization orientation of the electrodes. This is the basis of tunneling magnetoresistance (TMR). The definition of TMR is given as:

$$TMR = \frac{\Delta R}{R} = \frac{R_{AP}}{R_P} \quad (1.11)$$

$R_{P(AP)}$ indicates the resistance when the magnetization of the two FM electrodes are parallel (antiparallel). Manganites are used as a source of ferromagnetic layer in

magnetic TJ (Asamitsu et al., 1997; Teresa et. al., 1999a, 1999b, Worledge & Geballe, 2000; Jo et al., 2000).

1.6.2 Anisotropic magnetoresistance

Anisotropic magnetoresistance (AMR) appears in ferromagnetic materials, and is the dependency of the resistivity on the relative orientation of the magnetization and the current. The AMR effect depends on the distribution of magnetic domains, since the resistance of a domain with M parallel to the applied current I is different from the resistance of a domain with M perpendicular to I . In many materials, especially magnetic transition metals, the AMR effect is observed to vary as:

$$\Delta\rho = \rho_{\parallel} - \rho_{\perp} \quad (1.12)$$

where $\rho_{\parallel}$ is the resistivity when the current is parallel to the magnetization, and $\rho_{\perp}$ when they are perpendicular.

1.6.3 Ordinary Magnetoresistance

The ordinary magnetoresistance is related to the Hall effect and originates from the impact of the Lorentz-force on moving charge carriers. The change in resistivity, $\Delta\rho$, is positive for both magnetic field parallel $\Delta\rho_{(\parallel)}$ and transverse $\Delta\rho_{(\perp)}$ to the current direction with $\Delta\rho_{(\perp)} > \Delta\rho_{(\parallel)}$. The difference between $\Delta\rho_{(\parallel)}$ and $\Delta\rho_{(\perp)}$ is generally proportional to the applied magnetic field (McGuire & Potter, 1975). There are three distinct cases of ordinary magnetoresistance, depending on the structure of the electron orbitals at the Fermi surface: i) In metals with closed Fermi surfaces, the electrons are constrained to their orbit in k -space, applying a magnetic field increases the cyclotron frequency of the electron in its closed orbit. In this case the magnetoresistance saturates at very large magnetic fields. Metals which exhibit this behavior include In, Al, Na and Li. ii) For metals with equal numbers of electrons and holes, the magnetoresistance increases with applied field up to the highest fields measured, and is independent of crystallographic orientation. Bi, Sb, W

and Mo are some examples. iii) For metals that contain Fermi surfaces with open orbits in some crystallographic directions, large magnetoresistance will be exhibited for fields applied in those directions, whereas the resistance will saturate in the other directions, where the orbits are closed. This behavior is found in Cu, Ag, Au, Mg, Zn, Cd, Ga, Ti, Sn, Pb, and Pt (Nickel, 1995).

1.6.4 Extraordinary Magnetoresistance

More recently it has been observed that spatially inhomogeneous non-magnetic semiconductors can give rise to an extraordinary magnetoresistance which is discovered by Solin et al. (2000). He used a symmetric van der Pauw disk of homogeneous nonmagnetic indium antimonide with an embedded concentric gold inhomogeneity. The disk showed room-temperature geometric magnetoresistance as high as 100%, 9100%, and 750,000% percent at magnetic fields of 0.05, 0.25, and 4.0 T. This extraordinary magnetoresistance occurs in semiconductor metal hybrids where a magnetic field is applied perpendicular to the plane. With no magnetic field the current tends to flow through the metal (low resistance). However with an applied magnetic field the current is forced to flow through the semiconductor which is of much higher resistance (Green, 2011). Large magnetoresistance has also been demonstrated in point contacts between Ni crystals (García et al., 1999; Chopra & Hua, 2002).

1.6.5 Giant Magneto-Resistance (GMR)

The giant magnetoresistance (GMR) was discovered in thin film structures of Fe(001)/Cr(001) superlattices (Binasch et al., 1989; Baibich et al., 1988). The GMR phenomenon has had an enormous technological impact on the computer hard drive industry and has received even more attention with the recent Nobel Prize award in physics, which was given for GMR in 2007.

In the absence of an applied magnetic field, there is weak antiferromagnetic coupling between the adjacent stratum of ferromagnetic materials (separated by a non-magnetic layer). So a conduction electron travelling through this spacer layer

will have opposite spin to the site it is moving to. Hence the electrical resistivity of a material exhibiting giant magnetoresistance is at a maximum with zero external magnetic fields. If a magnetic field of sufficient magnitude is applied, all the spins in the ferromagnetic layers will align in a parallel fashion such that the inter-layer coupling is also ferromagnetic. In this case, conduction electrons may propagate easily through the spacer layers and the resistance is lowered (Nickel, 1995, Gerber et al., 1997).

2. EXPERIMENTAL METHODS

This chapter gives a brief overview of the experimental techniques used to prepare and characterize the Mn-based oxides. The details of the various commercially available instruments and home-built instruments used in the measurements of x-ray diffraction, magneto-electrical transport, a.c. susceptibility of the oxides are described.

2.1 Sample Preparation

There have been a great number of methods demonstrated till now to synthesize perovskite oxide materials. The most widely used methods are ceramic or solid state synthesis, sol-gel method, combustion, co-precipitation, etc. (Rao, 1994; West, 1999; Masala & Seshadri, 2004). While solid state synthesis is a high temperature technique, the others belong to the class of soft-chemical routes of synthesis. In this thesis, the lanthanum-based manganese oxides were prepared using the standard solid state synthesis method.

2.1.1 Solid State Synthesis Method

The most widely used method for preparing polycrystalline oxides is the direct reaction, in the solid state, of a mixture of solid starting materials. Powder solids are formed which can then be pressed and sintered to form dense polycrystalline pellets. Even though the desired phase is thermodynamically favored, solids do not usually react together at ambient temperature over laboratory time scales and it is necessary to heat the reactants at high temperatures to overcome the kinetic barriers. For such reactions, the rate limiting step is usually the solid state diffusion of the cations across the interface between the starting materials. In order to supply sufficient thermal energy to enable the ions to jump out of their normal lattice sites and diffuse through the crystal, high temperatures usually greater than 1273 K are required. Even at these temperatures, diffusion lengths are usually quite short. To

overcome from the this problem, the starting materials are usually ground to a fine powder, which both decreases the length the ions must travel and increases the surface area for reaction. The powders are often pressed into a pellet before heating to increase the contact between particles. Reaction times are usually several days and it is best to repeat the process to insure homogeneous samples.

The highly purified powders (>99.9 %, from the Alfa Aesar) of La_2O_3 , CaCO_3 , CaF_2 and MnO_2 are mixed in stoichiometric ratios, ground and calcined at 1173 K for 20 h. The remaining black powder was ground, pelletized and sintered for 20 h at 1323 K with two intermediate grindings. Finally the obtained pellets are reground, pelletized and annealed at 1623 K for 20 h. The details of the preparation procedure can be seen in Fig.2.1. The samples were prepared in high alumina combustion boat (Sigma Aldrich) using a high temperature furnace (Protherm, PLF 150/5) which has controlled heating and cooling options with temperature stability of $\pm 1^\circ\text{C}$.

2.1.2 Oxygen stoichiometry in bulk samples

The amount of oxygen has a crucial role on physical properties in manganites. The reliable results can only be achieved from stoichiometric samples where oxygen content is nominal (3 ± 0.01) (Franck et al., 2001). It was shown that at lower sintering temperatures, i.e. temperatures substantially lower than 1473 K, oxygen efficiency always exists. Franck and his group (2001) have optimized the sintering and oxygen exchange conditions to obtain samples with negligible oxygen efficiency or deficiency.

In this thesis, for pure samples, we have followed the same sample preparation conditions that described by Franck where an oxygen content close to 3.0 is expected. In order to further clarify the oxygen stoichiometry and content in our rest samples we have carried out iodometric titrations. The iodometry method used in this study is based on that described by Vogel (1964) and Yakel (1955).

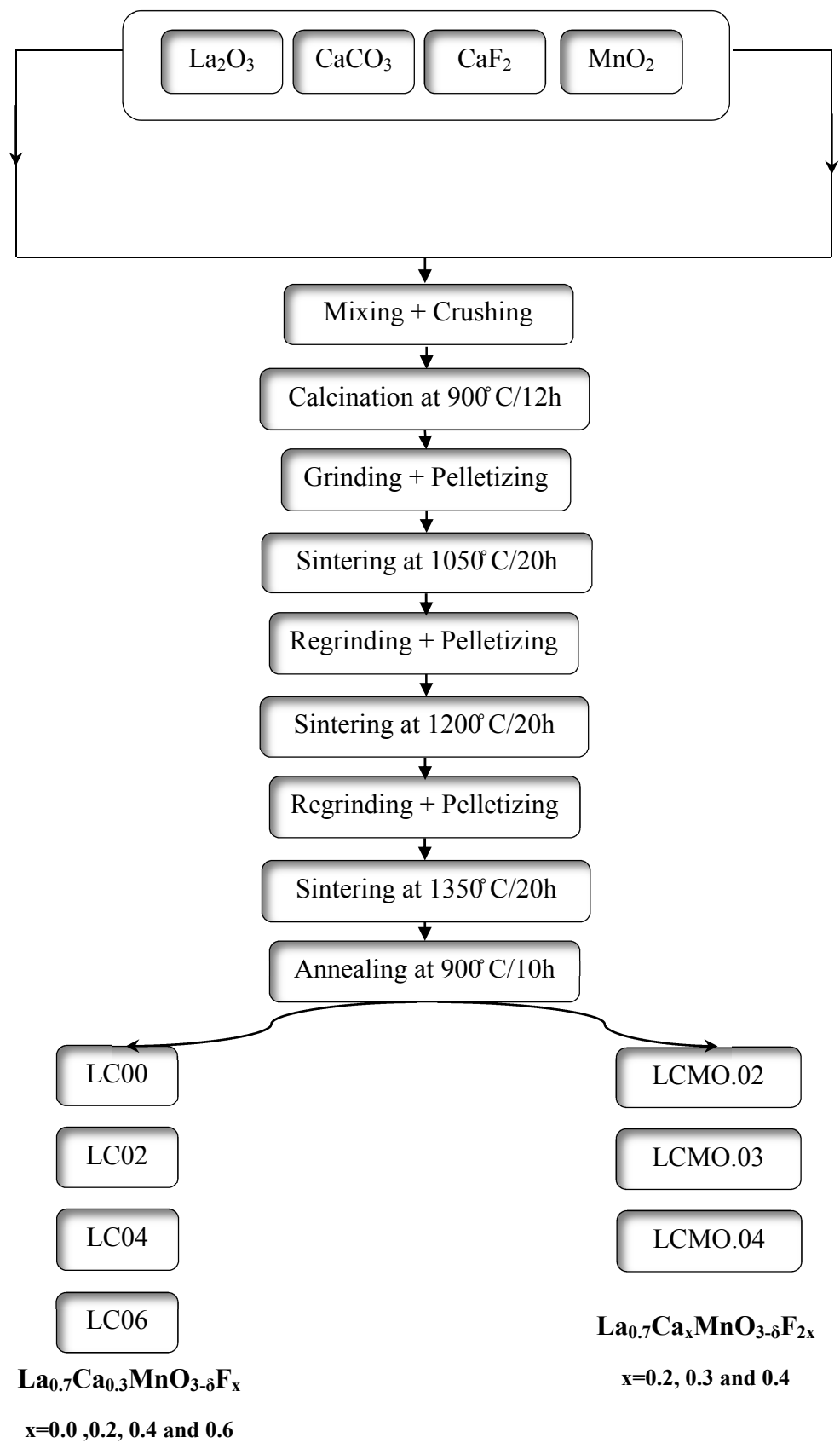


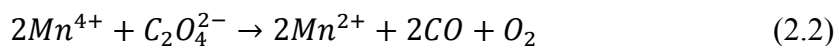
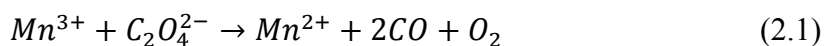
Figure 2.1. The sample synthesis procedure by the solid-state reaction method.

The analytical procedure of the iodometric titration is as follows:

We have prepared approximately 0.05 N KMnO_4 solution by dissolving 0.8 g commercial salts in distilled water (500 ml) and then boiled the solution for 1-2 h under gently heating. The solution was deposited in shady place for a whole night and preserved them in dark containers after filtered impurity in the solution.

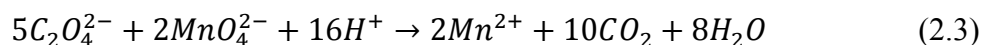
About 0.075 N $\text{Na}_2\text{C}_2\text{O}_4$ solution was obtained by dissolving dried salts (1 g) in 1:1 v/v H_2SO_4 (200 ml). The concentration of KMnO_4 solution above made was a new decided before the solution was used to titrate. Approximately 20 mL $\text{Na}_2\text{C}_2\text{O}_4$ standard solution was taken out using graduated flask and placed in 50 ml beaker. Then the solution was heated up 60-80 °C. The KMnO_4 solution in the buret was simultaneously dripped drop by drop into the $\text{Na}_2\text{C}_2\text{O}_4$ solution containing H_2SO_4 until a pink color in the KMnO_4 solution can keep 30 seconds and the temperature of the solution for the endpoint of titration is not under 60°C (See Fig. 2.2). At the end of the process, the concentration of KMnO_4 solution can be calculated as 0.086 N according to the amount of the $\text{Na}_2\text{C}_2\text{O}_4$ standard solution.

We have weighted approximately 0.2 g of the powder samples and placed in a beaker, then dissolved in (1+1) sulfuric acid containing an excess of sodium oxalate (20ml). The sealed crucible was laid in an oven under the temperature of 50 °C for 24 hour. So the powder samples for the hole-doped manganites $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_y$ reacted with a suitable excess of $\text{Na}_2\text{C}_2\text{O}_4$ (0.1g for 0.2g of sample), which deoxidize Mn^{3+} and Mn^{4+} to Mn^{2+} according to the quantitative reaction:



When the heat conservation was ended, we have added distilled water into beaker till 150 ml. The beaker was placed on the magnetic heating stirrer and stirred for about 10 minutes. Then the KMnO_4 solution above prepared in the buret was dripped drop by drop into the beaker until a pink color in the solution could keep 30 seconds and the temperature of the solution for the end-point of titration was not under 60°C. Note that the titration was carried out in the process of heating and

stirring at the same time (Yang et al., 2005). The unreacted $\text{Na}_2\text{C}_2\text{O}_4$ after finishing reaction 2.1 and 2.2 oxidized Mn^{7+} to Mn^{2+} according to the quantitative reaction:



So the oxygen content for the samples $\text{La}_{1-x}\text{Ca}_x\text{MnO}_y$ is then obtained as:

$$y = \frac{5-x}{2} + \frac{n_1-n_2}{n_3}, \quad (2.4)$$

where n_1 is the amount of total $\text{Na}_2\text{C}_2\text{O}_4$, n_2 is the amount of $\text{Na}_2\text{C}_2\text{O}_4$ reacted with KMnO_4 and n_3 is the amount of the powder samples.



Figure 2.2. A picture of the experimental iodometric titration set-up for determination oxygen stoichiometry.

2.2 Structural Analysis

2.2.1 X-ray diffraction (XRD)

We have used several techniques to characterize our samples and powder x-ray diffraction is probably the most important ones. This technique can be used for phase identification, particle and unit cell size determination. When an electromagnetic wave enters a crystal it will be scattered by the electrons inside. For certain angles of incidence there will be constructive interference between the different scatterers, but for most angles destructive interference will cancel the diffracted beams. By measuring at which angles the constructive interference occurs it is possible to learn about the geometrical ordering of the atoms inside the crystal (Cullity, 1978; Warren, 1969; James, 1948).

XRD can be used both to quickly identify which phases are present in an unknown sample and to perform a detailed structural investigation. In powder xrd, the sample consists of many small crystallites which are assumed to be randomly oriented. This produces rings of diffracted x-rays, defined by the angle between the incident and diffracted beams, 2θ . The atomic unit cell determines the condition of diffraction. In this method, the structure type of a material and unit cell size can easily be determined. If more than one type of material is present, the diffraction pattern will be a superposition of each of the components. If only phase identification is desired, this often provides enough information (Snyder & Simon, 1994; Klug & Alexander, 1974). XRD technique is based on the principle of Bragg's law of diffraction: $2d \sin\theta = n\lambda$ where, d is the spacing between the crystalline lattice planes, θ is the glancing angle between the incident X-ray beam and crystalline plane, n is the order of diffraction and λ is the wavelength of the incident X-ray beam. In this thesis, Rigaku powder X-ray diffractometer with Cu-K α radiation ($\lambda = 1.542\text{\AA}$) was used for the structural characterization of the polycrystalline compounds (see Fig. 2.3). The Rietveld refinement method was used to fit the measured powder XRD pattern of the compounds with the help of JANA in order to calculate the unit cell parameters. During our XRD experiments, the samples were scanned from $2\theta = 20^\circ$ to 80° with a scan rate of $3^\circ/\text{minute}$ and $0.5^\circ/\text{minute}$ for normal

(to confirm the phase formation of compounds) and slow scan (to fit the observed XRD pattern using Rietveld refinement in order to calculate the unit cell parameters) measurements, respectively.



Figure 2.3. A picture from Rigaku X-ray diffractometer system during the powder x-ray diffraction.

The Rietveld method is a powerful technique to extract detailed structural information from powder diffraction data (Rietveld, 1967, 1969). Contrary to the traditional profile fitting techniques, this method does not use integrated intensities of reflections but employs the entire powder diffraction pattern. In this method, each data point in the digitized intensity versus 2θ curve is an independent observation and during refinement, structure parameters, background parameters and profile parameters are varied in a least squares procedure until the simulated pattern matches well with observed pattern for the proposed structure model (Young, 1993).

2.2.2 Scanning Electron Microscope Imaging

A SEM is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with electrons in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron

beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image.

In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three dimensional appearance useful for understanding the surface structure of a sample. A wide range of magnifications is possible, from about 24 times (about equivalent to that of a powerful hand-lens) to more than 100,000 times. The SEM used in this work belongs to JSM 6390 LV-JEOL microscope, (see Fig. 2.4). The grain size and surface morphology of the all series were investigated by SEM operated at an acceleration voltage of 20 kV. The elemental composition and homogeneity of the all samples were investigated by means of quantitative energy dispersive x-ray spectroscopy (EDS) using the same SEM equipped with an x-ray detector. For composition detection the microscope was operated at 20 kV.



Figure 2.4. JEOL JSM-6390LV Scanning Electron Microscope.

2.3 Magnetic and Electrical Measurements

Magnetic properties of materials are derived from magnetization and susceptibility measurements in different kinds of magnetometer systems. The magnetization measurements were performed on a 7304 model Lake Shore Vibrating Sample Magnetometer (VSM) in Cukurova University's laboratory (see Fig. 2.5). A small part of the pellet (10-40 mg) is weighed and made tight to avoid movements inside the sample holder. The principle of VSM is the measurement of the electromotive force induced by magnetic sample when it is vibrated at a constant frequency in the presence of a static and uniform magnetic field. Different magnetic characterizations can be done with a VSM. In this thesis, we used VSM mainly to measure hysteresis loops at different temperatures with applied magnetic fields for the first serie. From hysteresis loops, information such as saturation magnetization (M_s), remanence (M_r), and coercivity (H_c) can be obtained. Also, we have analyzed the dependence of magnetization with temperature for the same serie.



Figure 2.5. 7304 model Lake Shore Vibrating Sample Magnetometer (VSM).

The basic home-made ac susceptibility system is depicted in Fig.2.6. A coil system comprises of a primary field coil (solenoid) and two secondary pickup coils

kept coaxially, are used to measure the ac susceptibility signal. These pickup coils are made identical and connected in series opposition. In this case, if a sinusoidal current is passed through the primary coil the voltage induced across the pick-up coils is nearly zero. If the sample is placed in one of the pick-up coils a net voltage having same frequency as the primary current will appear which is measured employing a lock-in amplifier. We have used Stanford research system lock-in amplifier (SR850 DSP) for voltage measurement. We used the voltage across a resistor connected in series with the primary coil as the reference voltage of the lock-in amplifier. Susceptibility is measured as a function of temperature for the materials. The samples under present investigations were also characterized by this technique to determine the magnetic transition temperature.



Figure 2.6. The cryostat assembly ac susceptibility system.

The low temperature DC conductivity of manganite sample was taken by cooling the sample using a closed cycled helium cryostat with a superconducting magnet solenoid (CRYO Industries - Model CF-2376-RTB) (Fig. 2.7). This system uses helium as the refrigerant and is designed to interface with many kinds of apparatus that requires cryogenic temperatures. The magnet is a close-cycle

cryocooled Nb₃Sn superconducting magnet and achieves a field up to 7 T. The temperature was controlled by using cryogenic temperature controller from Cryogenic Control Systems (Model 32B), which has a stability of 3 mK at 300 K. The pressure inside the cryocooler was maintained with the help of Varian Vacuum Pumping System Model 969-8227. Electrical resistance measurements are rather easy and straight forward to make and provide much useful information about the electrical properties of the sample. The measurements of electrical resistance as a function of temperature give information about the various temperature dependent electronic phase transitions. It also allows us an easily accessible and accurate value of the transition temperature as well as information of the quality of the sample. A low contact resistance is desirable due to the small resistance of the samples. For this aim we used standard four-probe method for measuring resistance of the samples. To measure the resistivity using this technique, the samples were cut in a rectangular bar shape using a fret-saw. Silver paint has been used for the electrical contacts of the probes with the sample. This silver paste is applied at the ends of the sample for current and mid points for voltage contacts. Due to very less resistance, thin copper wires were used with silver paint (see Fig. 2.8) and the whole assembly was put onto a sample holder, where the wires were connected with leads to the measurement instruments. As shown in the figure, current is passed through the outer probes (I₊ & I₋) and resultant potential difference developed between two points is measured using the inner probes (V₊ & V₋). The resistance can be calculated using the ohm's law $V = IR$, where I is the current passed and V is the voltage developed. It is imperative to keep the voltage probes between the current probes in a linear way. Using dimensions, shown in the same figure, the exact resistivity (ρ) of the sample can be calculated using the relation

$$\rho = R \frac{A}{l} \quad (2.1)$$

where R is the resistance, $A = w \times t$ is the cross-sectional area of the sample (w : width, t : thickness) and l is the shortest distance between the voltage probes. The samples were cooled down to 10 K by using He gas. The samples were then heated in a controlled way by using a heater and resistance was measured with slowly increasing temperature.

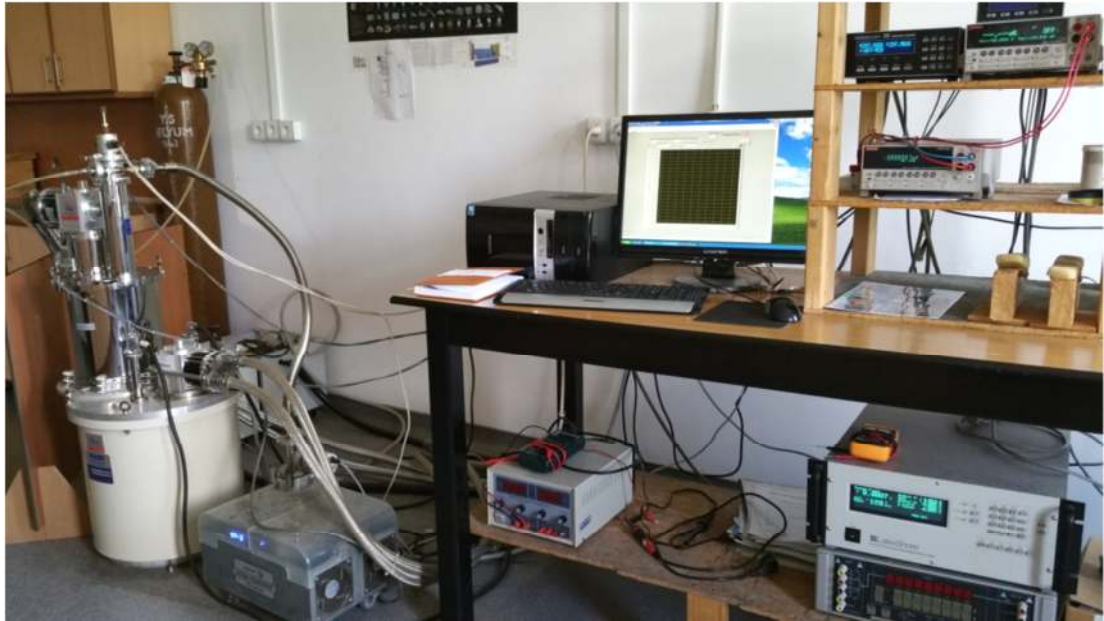


Figure 2.7. He gas contact cryocooler and superconducting coil magnet from CRYO Industries.

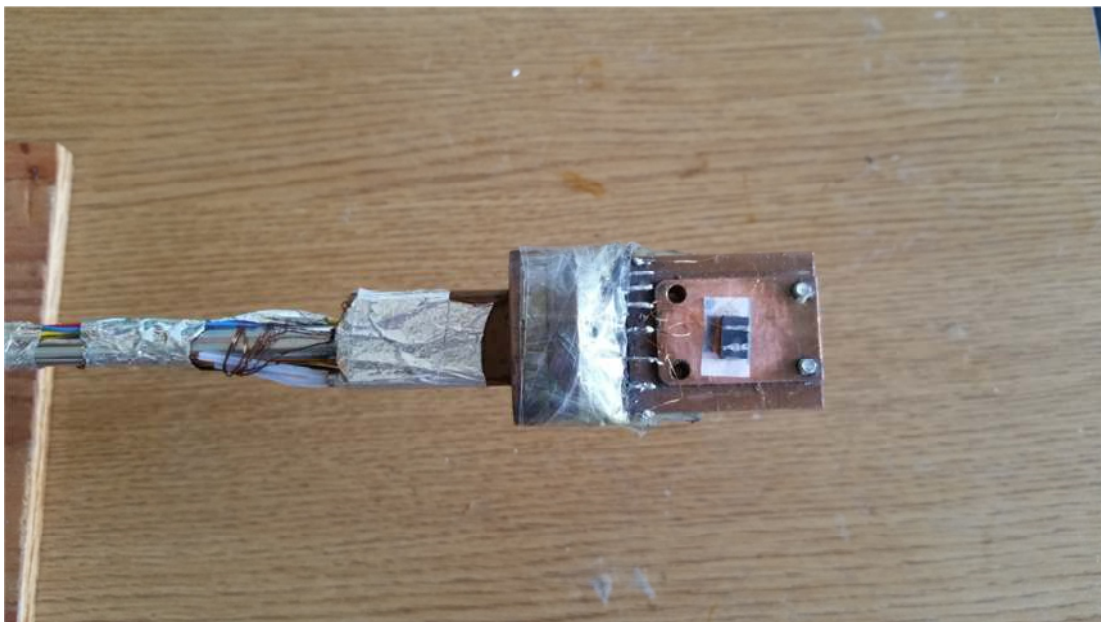


Figure 2.8. Experimental set-up for the 4-point probe measurement.

3. RESULTS AND DISCUSSION

Fig. 3.1 shows the powder x-ray diffraction diagrams of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ with $x = 0.0, 0.2, 0.4$ and 0.6 . It is clear from the figure that both of the samples exhibit the characteristic peaks of the perovskite structure with no detectable impurity. One can see from the inset of the same figure that the main diffraction peak at $\sim 32.5^\circ$ shifts gradually to lower angles with F doping which implies a possible change in lattice parameters. A typical plot of XRD patterns of samples along with their Rietveld refined ones are shown in Fig 3.2. The refinement of cell parameters was done in the orthorhombic system with Pbnm space group. Details of the procedure are as follows. The experimental intensities are fitted by use of pseudo-Voight function. A 36 terms of Legendre polynoms was used to describe the background and the Simpson method was applied for the asymmetry correction. The refined cell parameters as well as the obtained quality factors (R_p , R_{wp}) and the goodness of fit (GOF) are listed in Table 3.1. The lattice parameters and unit cell volume increase slightly with fluorine doping. It is well known that the ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ depends strongly on the oxygen content. Since Mn^{3+} ions are Jahn-Teller ions, they include a distortion of the MnO_6 octahedra and this distortion leads to enlarge the unit cell. Since the ionic radius of Mn^{3+} ($0.78 \text{ \AA}$) is much larger than that of Mn^{4+} ($0.67 \text{ \AA}$), the lattice constants increase with less oxygen content. Therefore, the average ionic radius increases with the number of Mn^{3+} ions (Zhao et al., 1999). As given in Table 3.1, the oxygen content of samples are estimated to be around 3.0, and 2.89 for LC00 and LC06 samples, respectively. It should be noted that compositional characterization by means of standard redox titration method indicates the stoichiometry of pure sample to be practically equal to the nominal one.

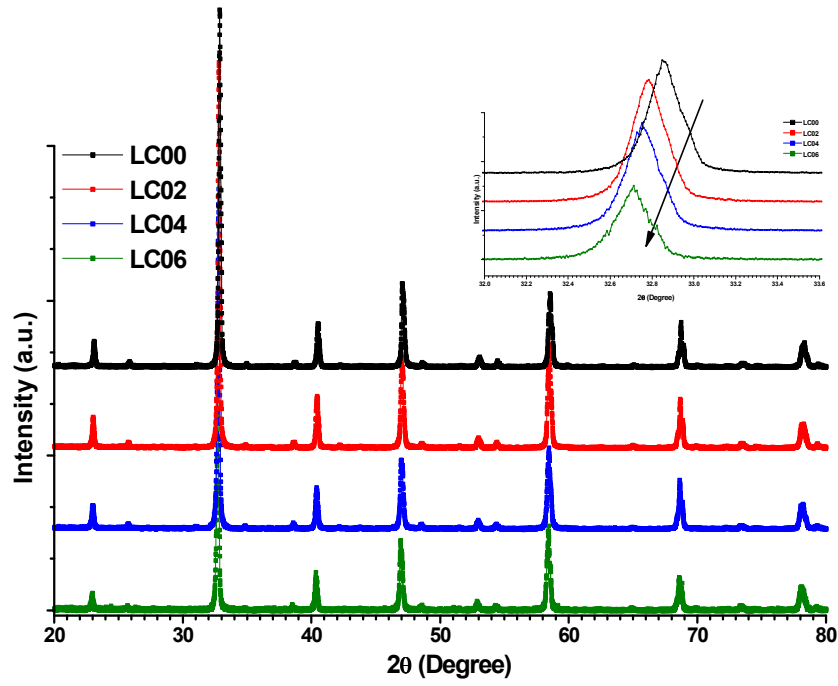


Figure 3.1. X-ray diffraction pattern of the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ compounds with $x = 0.0, 0.2, 0.4$ and 0.6 , measured at room temperature. Inset shows the main peak shift with doping.

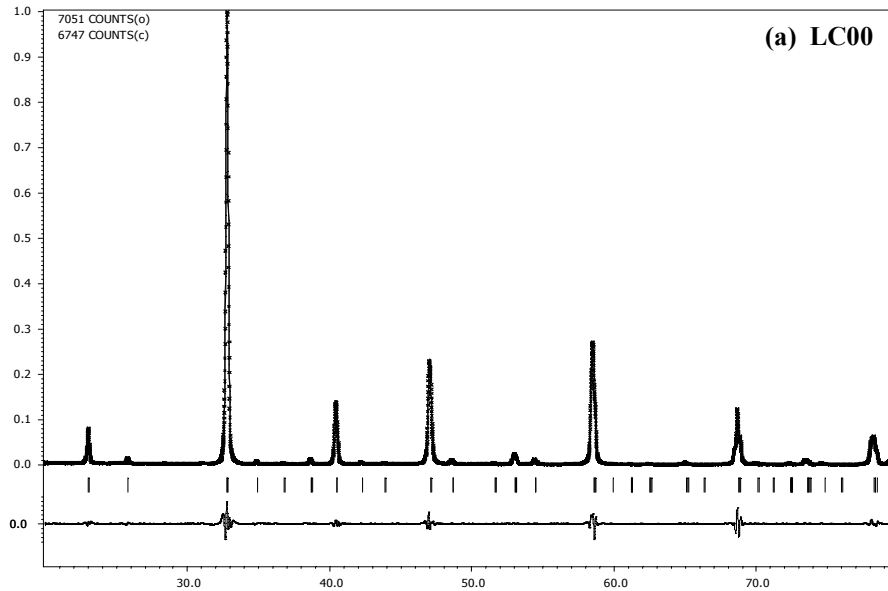


Figure 3.2. Rietveld profiles considering Pbnm space group for samples $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$ and (d) $x = 0.6$ (continued).

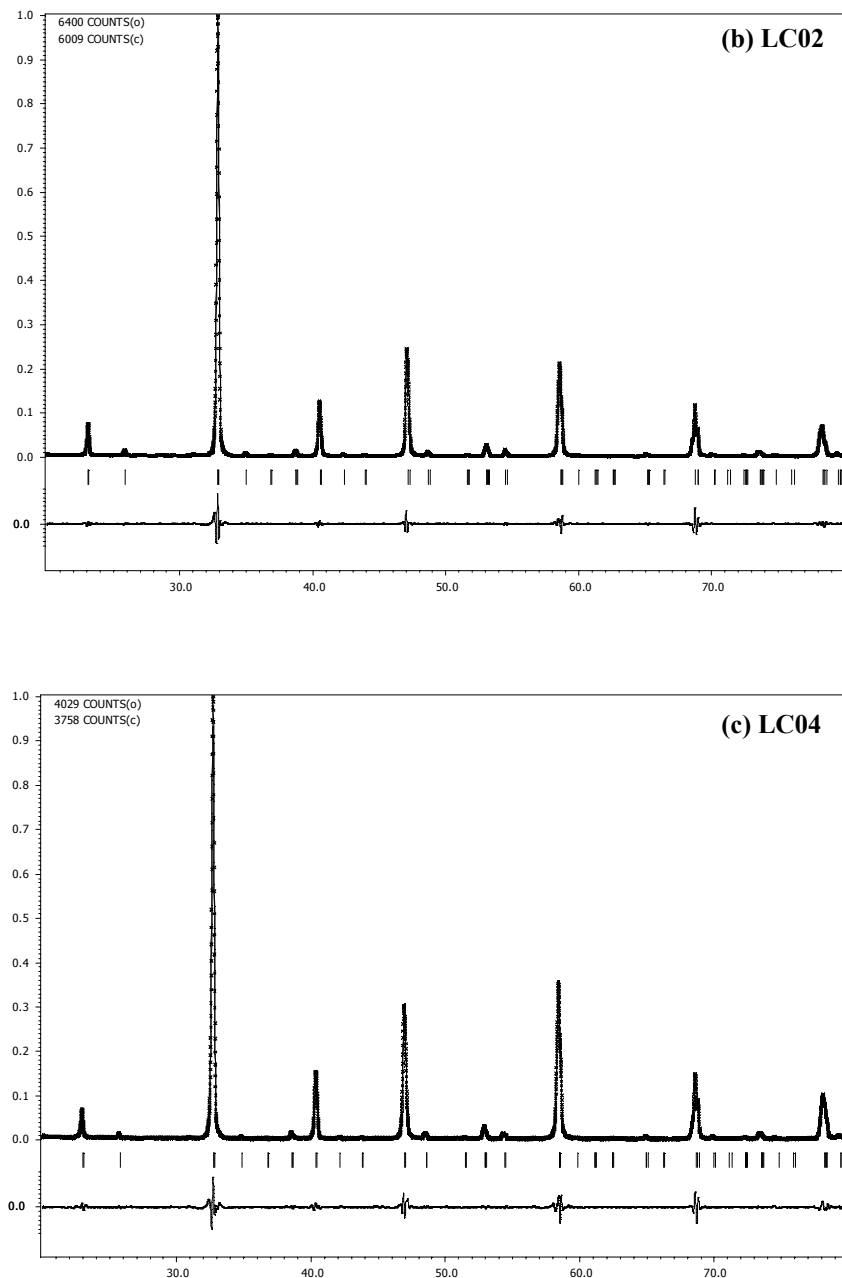


Figure 3.2. Rietveld profiles considering Pbnm space group for samples $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ **(a)** $x = 0.0$, **(b)** $x = 0.2$, **(c)** $x = 0.4$ and **(d)** $x = 0.6$ (continued).

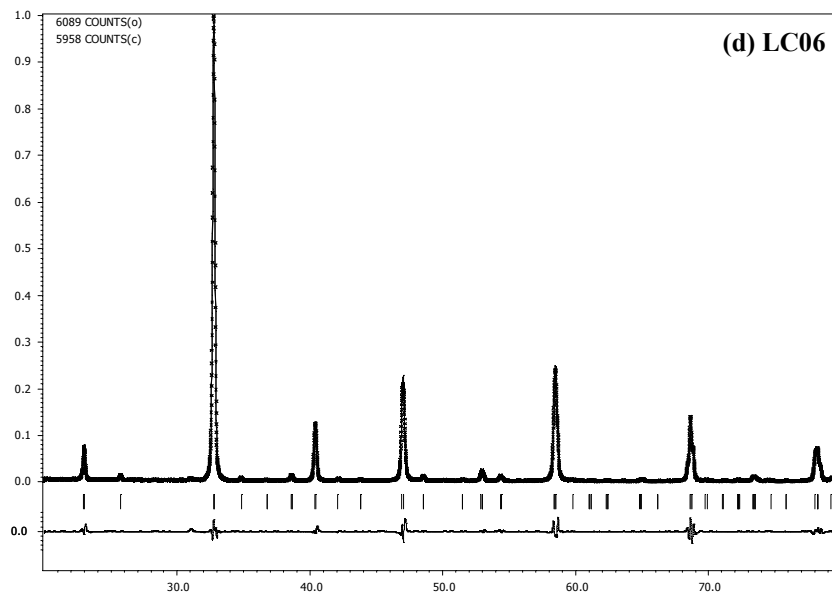


Figure 3.2. Rietveld profiles considering Pbnm space group for samples $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$ and (d) $x = 0.6$.

The typical SEM images of all samples are shown in Fig. 3.3. It is evident from the images that both samples have similar surface topography from the point of view. Since LC00 sample has some porosity, the connection of grains of LC06 sample is denser than that of LC00 sample. It should be noted that the grain size of LC00 and LC06 samples are about $20\mu\text{m}$ and does not depend on the dopant.

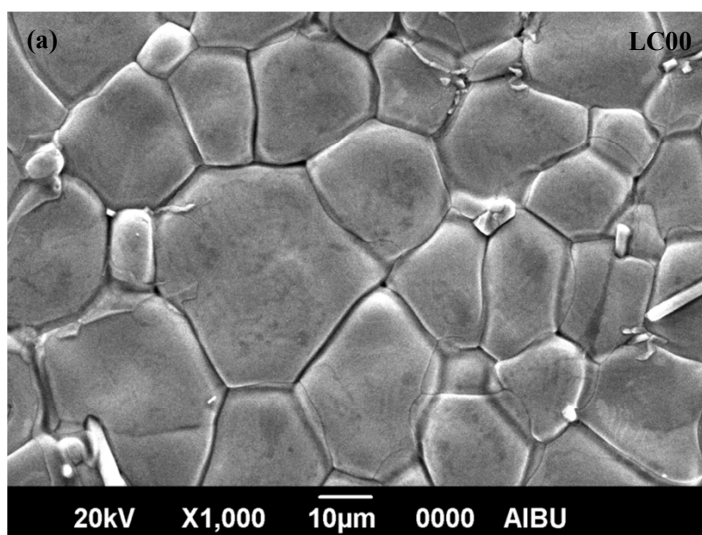


Figure 3.3. SEM micrographs of the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ compounds with $x = 0.0$, 0.2 , 0.4 and 0.6 (continued).

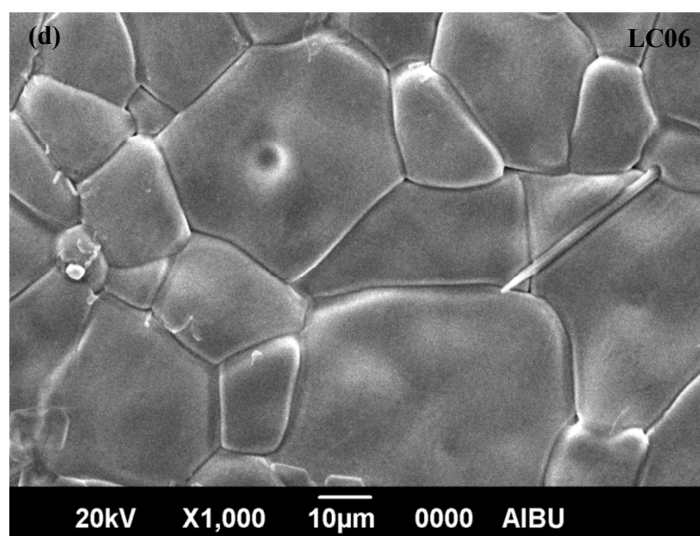
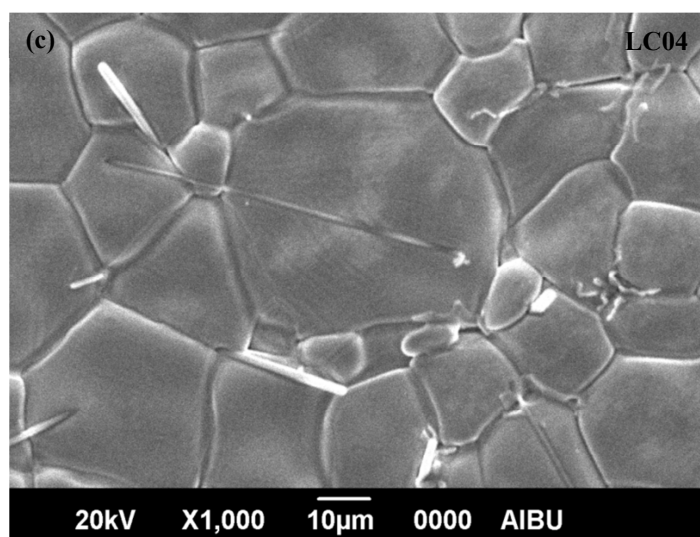
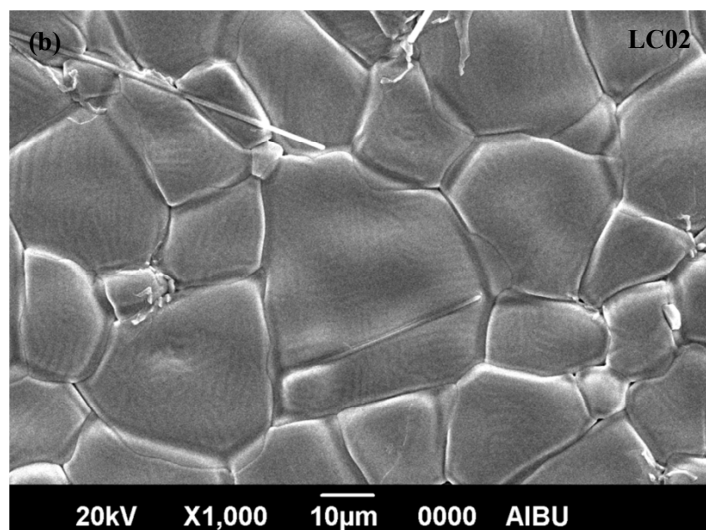


Figure 3.3. SEM micrographs of the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ compounds with $x = 0.0$, 0.2, 0.4 and 0.6.

Table 3.1. Rietveld refinement parameters of XRD pattern and the obtained experimental data of $La_{0.7}Ca_{0.3}MnO_{3-\delta}F_x$ with $x=0.0, 0.2, 0.4$ and 0.6 .

Sample	$La_{0.7}Ca_{0.3}MnO_{3-\delta}$	$La_{0.7}Ca_{0.3}MnO_{3-\delta}F_{0.2}$
Sample Code	LC00	LC02
a (Å)	5.457	5.460
b (Å)	5.450	5.455
c (Å)	7.697	7.699
V (Å)³	228.9	229.3
δ	0.0	0.07
R_p, R_{WP}	8.57, 12.54	9.94, 12.60
GOF	1.17	1.04
Space Group	Pbnm	Pbnm
T_C (K)	258	264
T_{MI} (K)	260	265
MR% around T_{MI} for 7T field	66	61

	$La_{0.7}Ca_{0.3}MnO_{3-\delta}F_{0.4}$	$La_{0.7}Ca_{0.3}MnO_{3-\delta}F_{0.6}$
Sample Code	LC04	LC06
a (Å)	5.465	5.468
b (Å)	5.452	5.451
c (Å)	7.710	7.745
V (Å)³	229.7	230.9
δ	0.08	0.11
R_p, R_{WP}	9.45, 12.14	7.77, 11.7
GOF	1.10	1.04
Space Group	Pbnm	Pbnm
T_C (K)	263	269
T_{MI} (K)	267	276
MR% around T_{MI} for 7T field	64	68

Fig. 3.4 shows the temperature dependence of magnetization of both samples under zero-field cooling (ZFC) and field-cooling (FC) modes from room temperature down to 10 K under a magnetic field of 10 mT. It is clear from the graphs that LC00 sample displays paramagnetic-ferromagnetic (PM-FM) phase transition at 258 K and that of Curie temperature gradually shifts at 269 K by fluorine doping (see also Table 3.1).

The doping by fluorine increases T_C value and supports that it takes part in the ferromagnetic-DE interaction. The increment in lattice parameters by F doping may also lead to increase the Curie temperature. Moreover, it is obvious from the figure that all samples display a clear bifurcation between ZFC and FC magnetization branches at a temperature very close to the T_C which implies the existence of a glassy magnetic state. Indeed, the irreversibility in the M-T curve between FC and ZFC measurements is usually observed in hole-doped manganite systems and the reason of this thermal irreversibility is explained by the light of canted nature of the spins or the random freezing of spins (Dey et al., 2008; Zhao et al., 2009).

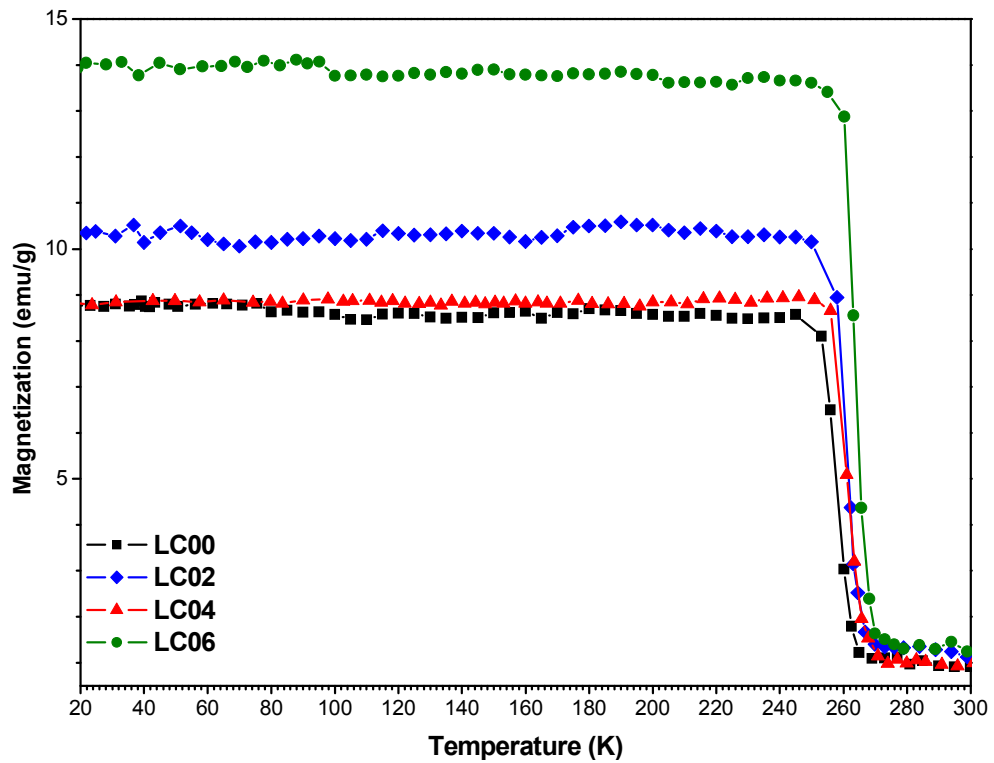


Figure 3.4. Magnetization-temperature curves, recorded in zero field cooled (ZFC) magnetization for samples $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ with $x = 0.0, 0.2, 0.4$ and 0.6 measured in magnetic field of 10 mT.

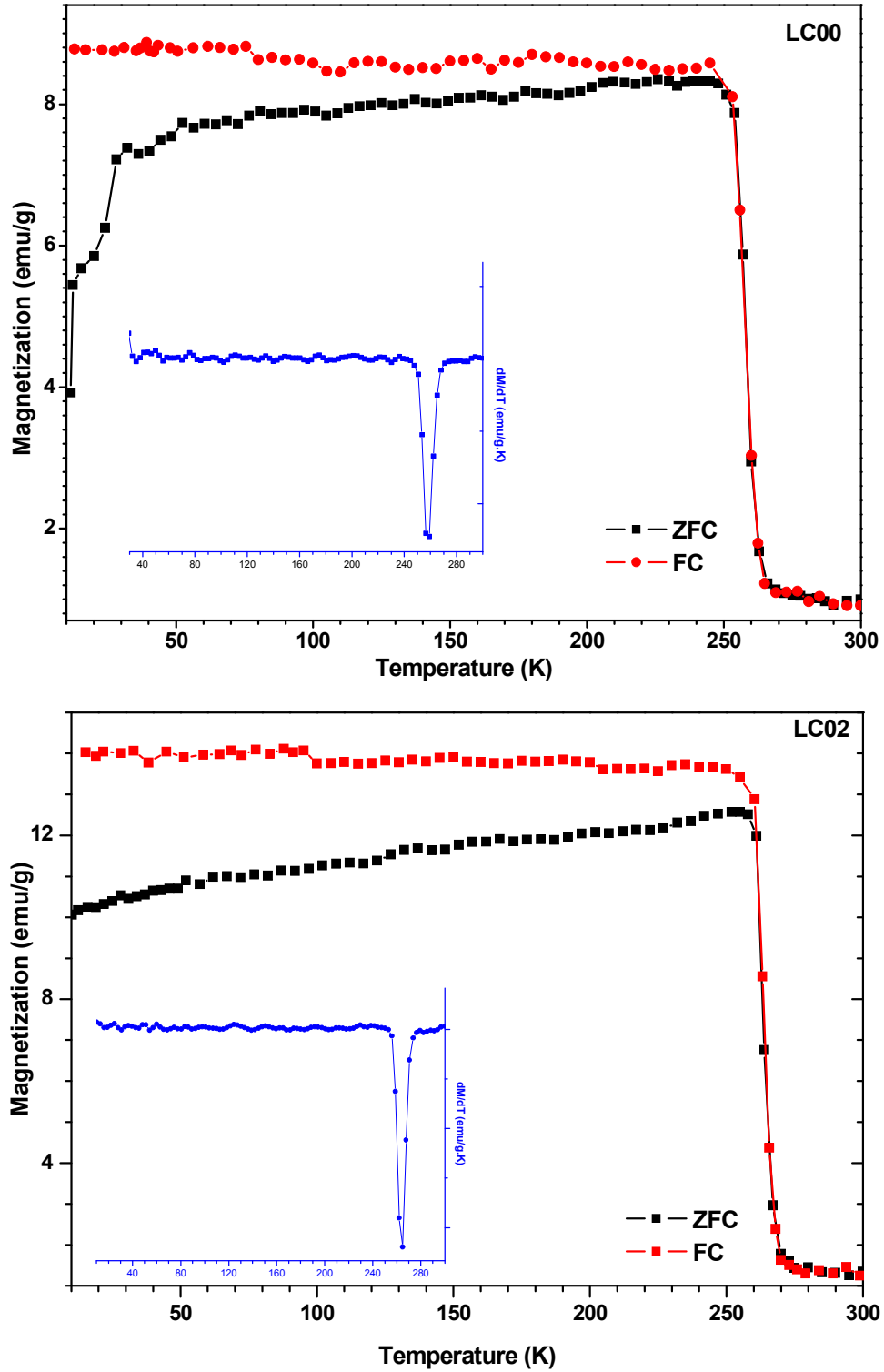


Figure 3.5. Magnetization-temperature curves, recorded in zero-field-cooled (ZFC) and field-cooled-magnetization for samples $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ with $x = 0.0, 0.2, 0.4$ and 0.6 measured in magnetic field of 10 mT. The insets show dM/dT vs T . (continued)

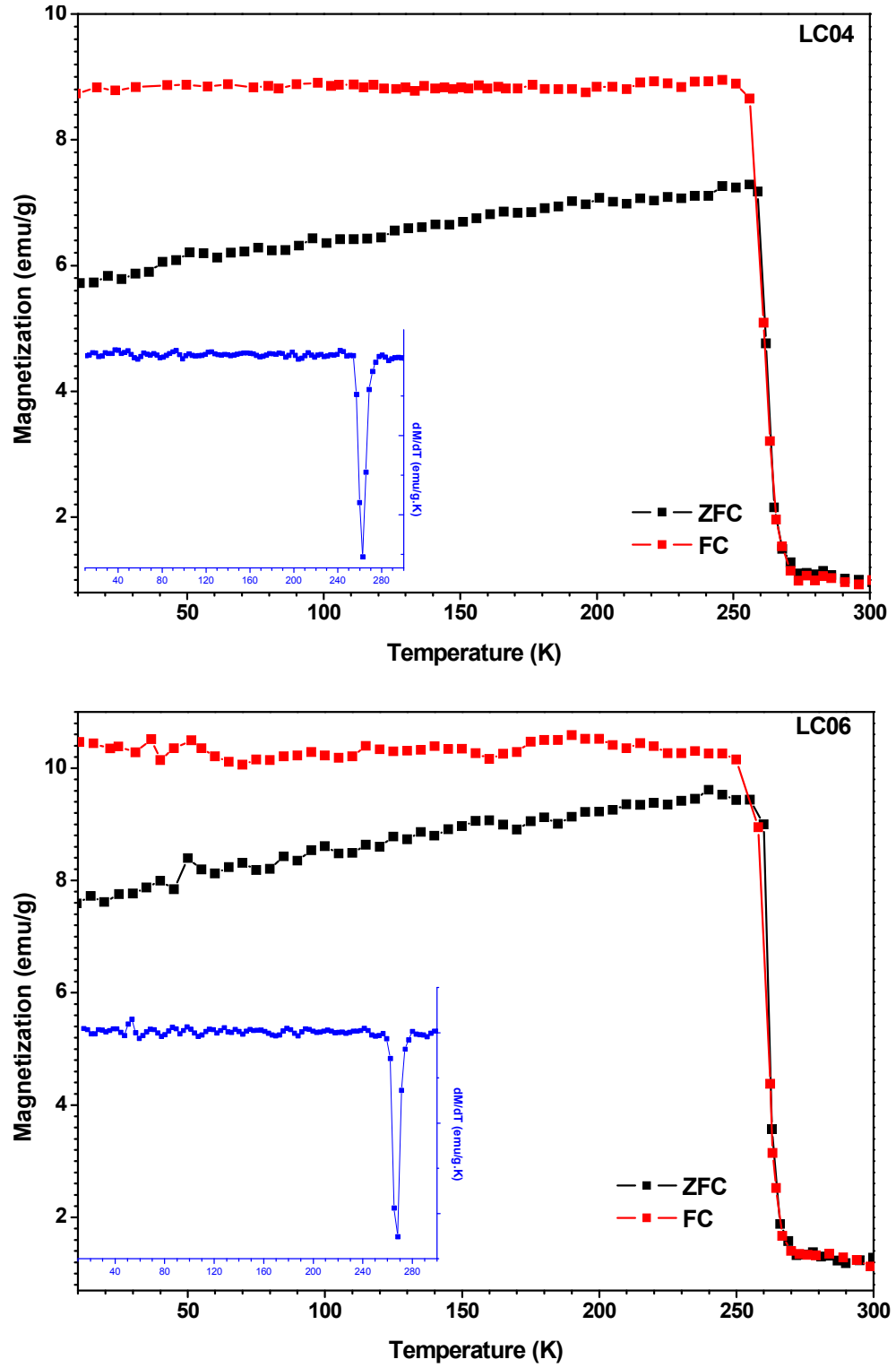


Figure 3.5. Magnetization-temperature curves, recorded in zero-field-cooled (ZFC) and field-cooled (FC) magnetization for samples $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ with $x = 0.0, 0.2, 0.4$ and 0.6 measured in magnetic field of 10 mT. The insets show dM/dT vs T .

Figure 3.6 is a plot of the hysteresis curve $M(H)$ measured over the same H range and at the same temperature (10 K). This curve measures the magnetic response of the samples, which is in the ferromagnetic state. At the coercive field H_{co} , of the samples, i.e. $M(H) = 0$, the density of domain walls is highest, while at the saturation field there is only one domain. Hence, the number of domains increases with increasing H from -10 dT to H_{co} , and it decreases with further increasing H . The high density of domain walls at $M(H) = 0$ leads to large stray fields since stray fields generally originate from domain walls within the FM layer (Steiner et al., 2006). The magnetization of all the samples nearly saturates above 0.5 T. The hysteresis in the M – H curve for all samples, along with the saturation, clearly confirms that we have a ferromagnetic state at low temperatures. It can be clearly seen that both the coercive field ($\mu_0 H_c$) and the remanant magnetization (M_R) is maximum for maximum fluorine doped sample ($x=0.6$).

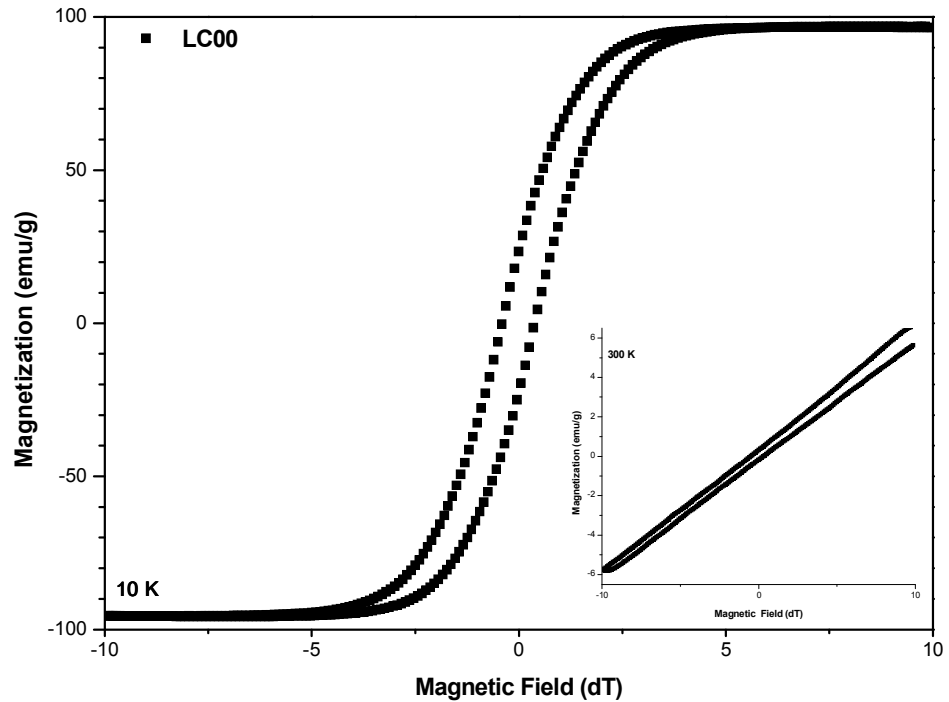


Figure 3.6. The isothermal magnetization, $M(H)$, curves for samples $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ with $x = 0.0, 0.2, 0.4$ and 0.6 measured at 10 K. The insets for samples LC00 and LC06 show M - H curves at room temperature. Note that dT indicates deciTesla. (continued)

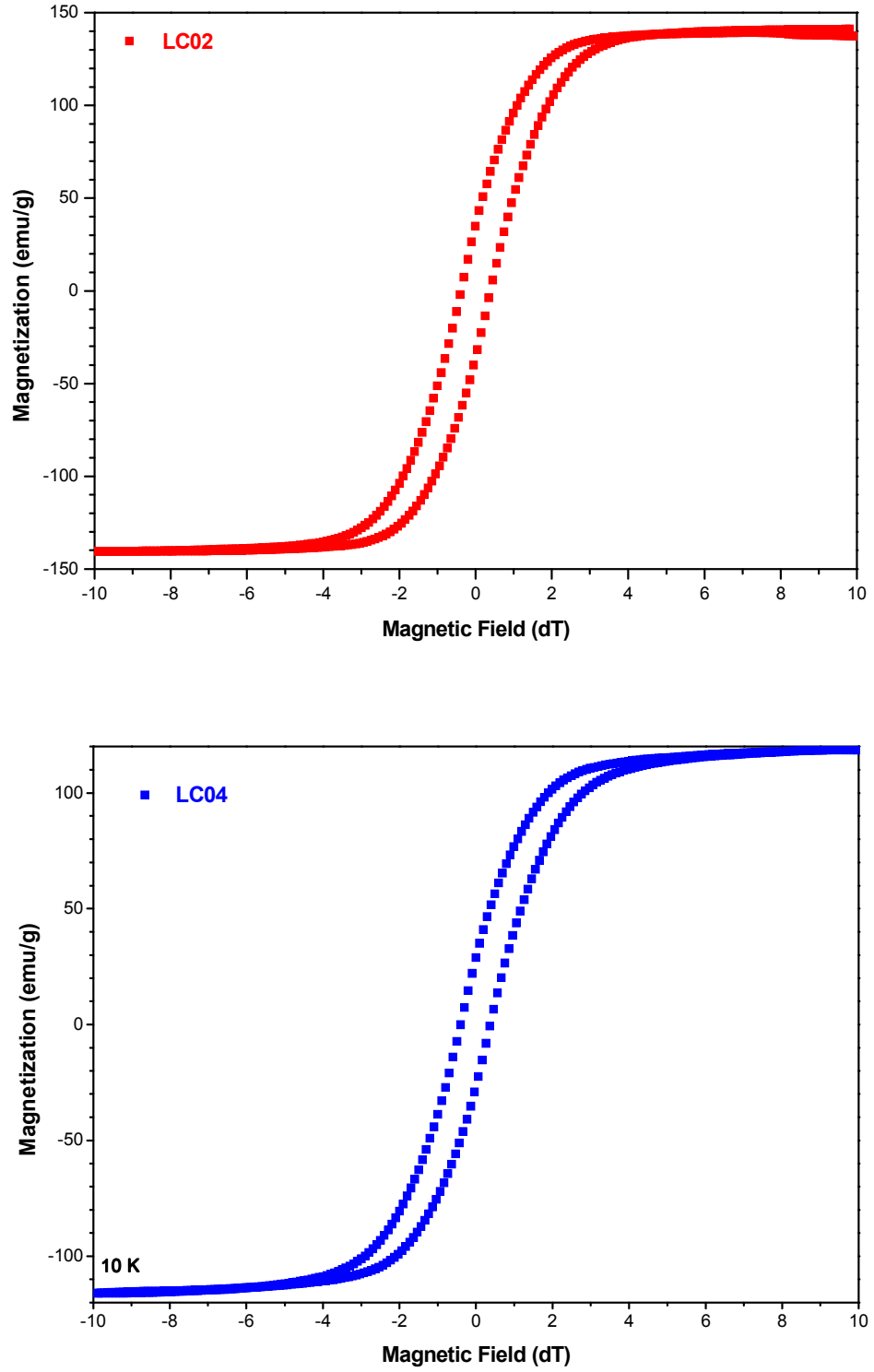


Figure 3.6. The isothermal magnetization, $M(H)$, curves for samples $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ with $x = 0.0, 0.2, 0.4$ and 0.6 measured at 10 K. The insets for samples LC00 and LC06 show M - H curves at room temperature. Note that dT indicates deciTesla. (*continued*)

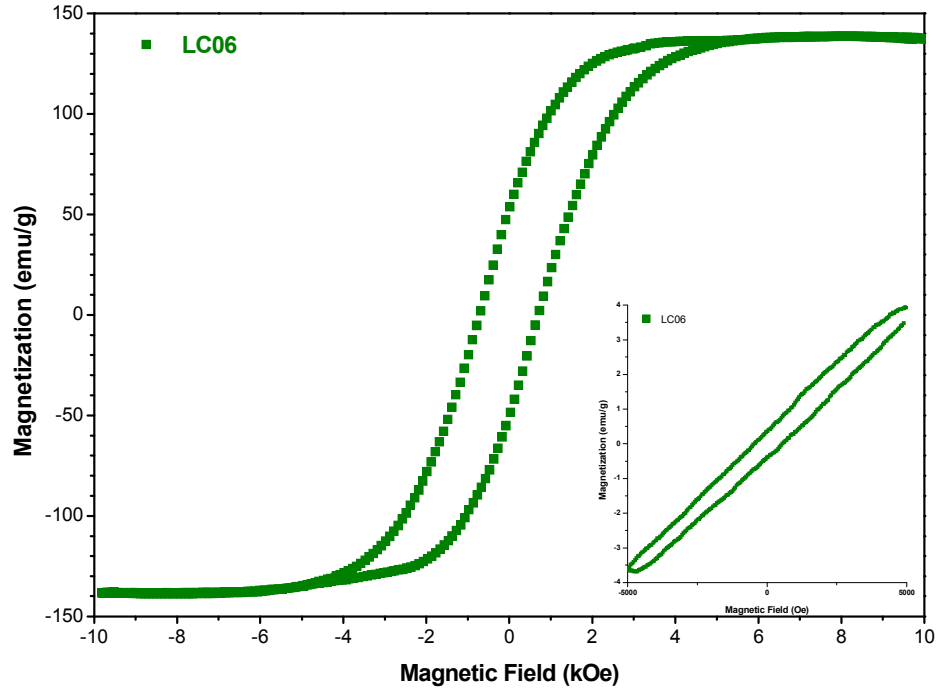


Figure 3.6. The isothermal magnetization, $M(H)$, curves for samples $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ with $x = 0.0, 0.2, 0.4$ and 0.6 measured at 10 K. The insets for samples LC00 and LC06 show $M-H$ curves at room temperature. Note that dT indicates deciTesla.

An impressive change of the magnetic behavior is strictly related to the electrical property of the hole-doped manganites. The temperature-dependent resistivity curves of both samples under zero magnetic field is displayed in Fig. 3.7. One obvious remark is that the resistivity undergoes a transition characterized by the resistivity maximum from the ferromagnetic metallic to the paramagnetic insulating state. The metal-insulator transition temperatures of samples (T_{MI}) are listed in Table 3.1 and one can see that the T_{MI} and T_{C} are correlated well with each other. Previous works on hole-doped manganites have shown that, T_{MI} and T_{C} correlate well only when the sample has large grain size with a ferromagnetic state associated with long range order (Mahenrian et al., 1996; Das & Dey, 2006).

Beside of this, we have also performed the temperature dependence of resistivity measurements in the presence of various magnetic fields ranging from 0 to 7 T (Fig. 3.8). It should be noted that, the peak in the resistivity curves tends to shift toward higher temperatures and decrease in magnitude with increasing the strength of the field. For this reason, the T_{MI} values are found to change in the range of 260-275 K for the LC00 and 276-294 K for LC06 sample when the field is changed from

0 to 7 T. The application of magnetic field partially causes the local ordering of magnetic spins by delocalizing charge carriers. Due to this ordering, the ferromagnetic region of the system is enhanced by suppressing paramagnetic region. Therefore, the T_{MI} shifts to high temperature regime with application of magnetic field (Venkataiah et al., 2005, 2007). Cao et al. (2000) also explained this phenomenon in terms of ferromagnetic clusters and domains.

To further understand the effect of magnetic field, the magnetoresistance calculations were performed for both samples in the full temperature range for the magnetic field of 7 T (see insets of Fig. 3.8). The MR values are calculated by using the well-known relation (Rao & Raveau, 1998), $MR\% = [\rho_0 - \rho_H] / \rho_0 \times 100$, where ρ_H and ρ_0 are the resistivities in non-zero and zero applied magnetic fields, respectively. The maximum of MR values are found to be 66% for LC00 sample and 68% for LC06 sample (Table 3.1). It should be noted that the maximum MR values are obtained around the transition temperature for both samples and are not affected significantly by doping.

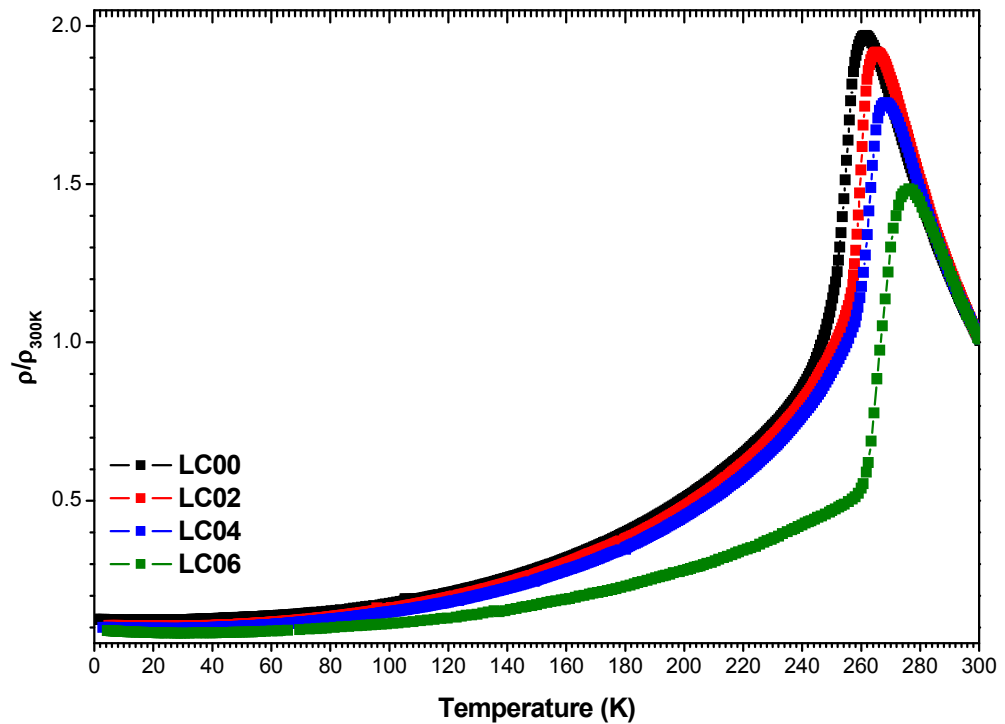


Figure 3.7. Temperature dependence of resistivity in zero field for samples $La_{0.7}Ca_{0.3}MnO_{3-\delta}F_x$ with $x = 0.0, 0.2, 0.4$ and 0.6 .

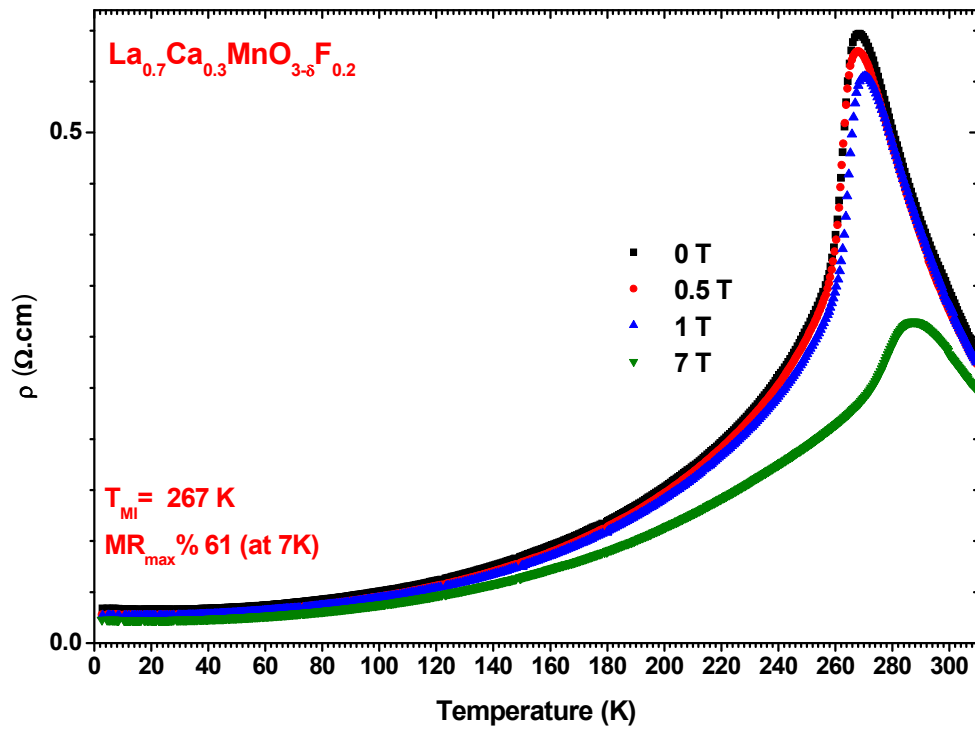
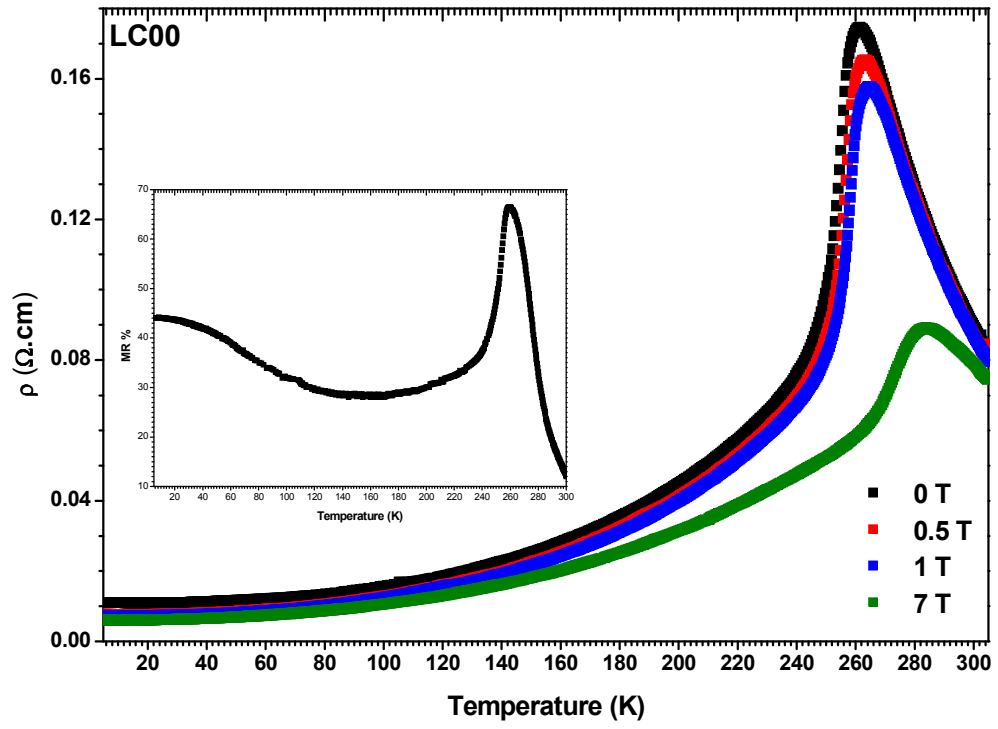


Figure 3.8. Temperature dependence of the electrical resistivity under applied magnetic fields 0, 0.5, 1 and 7 T, respectively for all samples. The MR ratio, calculated for 7 T, are displayed in the corresponding insets for LC00 and LC06. *(continued)*

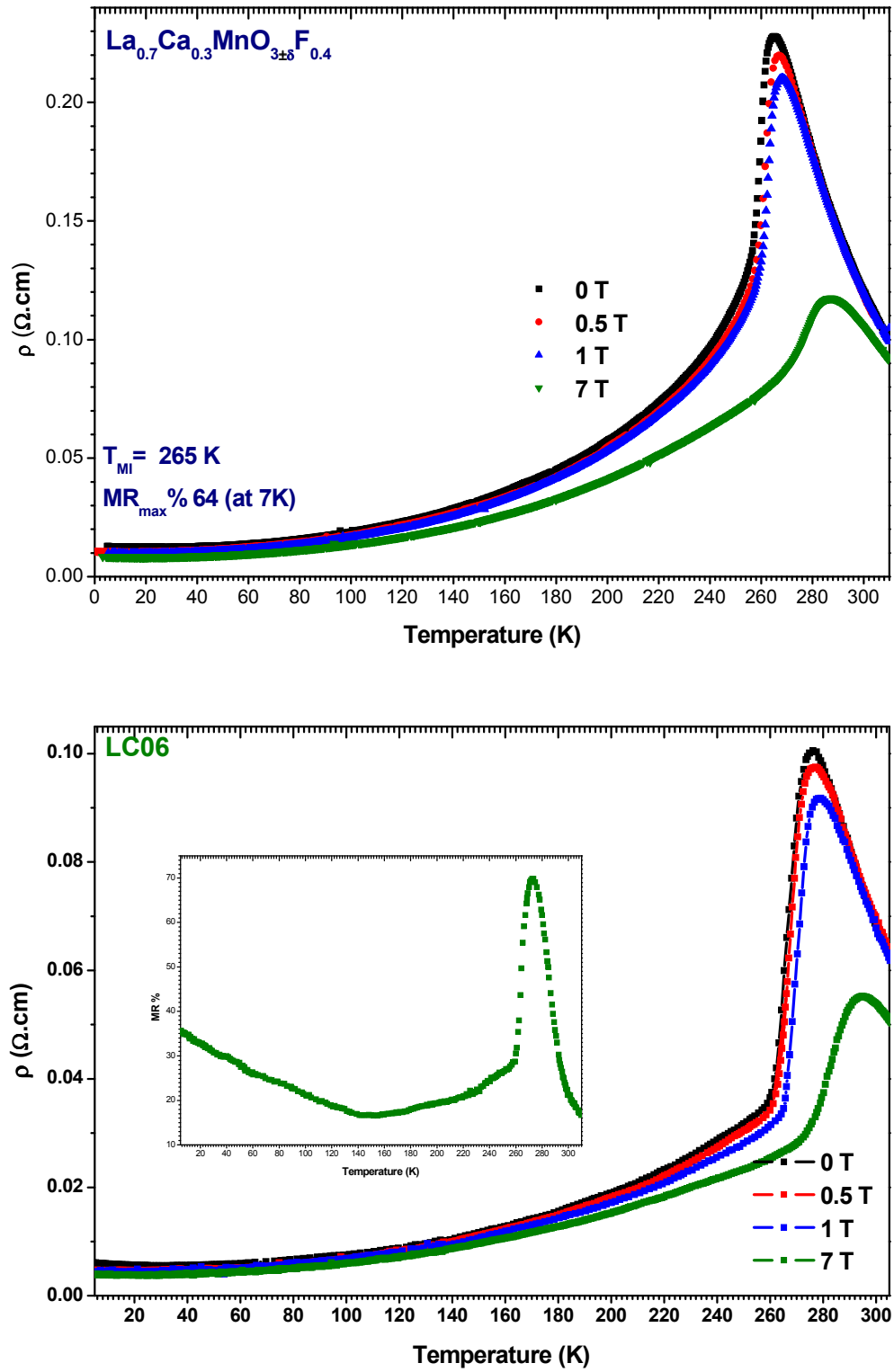


Figure 3.8. Temperature dependence of the electrical resistivity under applied magnetic fields 0, 0.5, 1 and 7 T, respectively for all samples. The MR ratio, calculated for 7 T, are displayed in the corresponding insets for LC00 and LC06.

4. MAGNETO-TRANSPORT CHARACTERIZATION

The powder X-ray diffraction and Rietveld refinement of the data of the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ with $x=0.0$ (LC00) and 0.6 (LC06) indicate that the samples have orthorhombic structure with Pbnm space group. The refined lattice parameters were obtained as $a = 5.457 \text{ \AA}$, $b = 5.450 \text{ \AA}$ and $c = 7.697 \text{ \AA}$ for pure sample and $a = 5.468 \text{ \AA}$, $b = 5.451 \text{ \AA}$ and $c = 7.745 \text{ \AA}$ for fluorine doped sample (Altintas et al., 2014).

The electrical conduction is apparently the most fascinating physical property of the CMR manganites. Magnetoresistance measurements were carried out in the presence of 0, 0.5, 1 and 7 T magnetic fields. The resistivity versus temperature curves at various applied fields is shown in Fig. 4.1. In order to explain the electrical transport behavior in these CMR manganites, we can categorize the temperature dependence of resistivity into two parts: low temperature $T < T_{\text{MI}}$ and high temperature $T > T_{\text{MI}}$ behaviors. Low temperature resistivity data are fitted with a general power law:

$$\rho_{FM} = \rho_0 + \rho_2 T^2 + \rho_{4.5} T^{4.5} \quad (4.1)$$

In the equation, ρ_0 is the temperature independent residual resistivity which appear due to the grain/domain boundary effects, scattering by impurities, defects and domain walls (Snyder et al., 1996; De Teresa et al., 1996). The term $\rho_2 T^2$ represents the electrical resistivity due to electron-electron scattering interaction (Banerjee et al., 2001; Urushibara et al., 1995), while $\rho_{4.5} T^{4.5}$ is attributed due to the process of electron-magnon scattering in the ferromagnetic region (Urushibara et al., 1995). For the high temperature conduction region ($T > T_{\text{MI}}$), the paramagnetic-insulating phase is controlled by the hopping motion of small polarons. The resistivity in this temperature region is expressed by adiabatic small polaron hopping (SPH) mechanism (Ziese, 2003; Varshney et al., 2010; De Andres et al., 1999) and the equation is given by:

$$\rho_{PM} = \rho_\alpha T \exp\left(\frac{E_p}{k_B T}\right) \quad (4.2)$$

In the SPH model, E_p represents the polaron activation energy, ρ_α is residual resistivity which is defined as $\rho_\alpha = 2k_B/3ne^2a^2\gamma$, here k_B is Boltzmann's constant, e is the electron charge, n is the number density of charge carriers, a is site-to-site hopping distance and γ is the longitudinal optical phonon frequency.

Unfortunately, none of the models above can explain the prominent change of the $\rho(T)$ curves at near metal-insulator transition temperature. Thus, for such a phase-foliated system, considering a percolation character of the metal-insulator transition, one can write a formulation for the resistivity behavior in the entire temperature range as:

$$\rho(T) = \rho_{FM}f + \rho_{PM}f' \quad (4.3)$$

where f and f' are the volume concentrations of the FM domains and PM regions, respectively and are given as:

$$f = \frac{1}{1 + \exp(\frac{\Delta U}{k_B T})} \quad (4.4)$$

and,

$$f' = 1 - f = \frac{\exp(\frac{\Delta U}{k_B T})}{1 + \exp(\frac{\Delta U}{k_B T})} \quad (4.5)$$

where $\Delta U = -U_0(1 - \frac{T}{T_C^{mod}})$, ΔU is the difference in energy between the FM and PM states and T_C^{mod} means a temperature used in the model near/equal to T_C . One can see the experimental (dashed lines) and simulated (solid lines) results for the ρ - T curves obtained at 0, 0.5, 1 and 7 T magnetic fields for doped and undoped samples in Fig. 4.1. The fit parameters for all samples obtained from Eqs: 4.1, 4.2 and 4.3 are listed in Table 4.1. We can obviously conclude that the model yields quantitative fits to the experimental data in the temperature range between 5 and 300 K at various applied magnetic fields. Consequently, T_C^{mod} is close to the T_{MI} . These concurrences approve that FM and PI regions coexist near T_{MI} . Moreover, one can see from the table that the activation energy values are decreasing with increasing magnetic field. Since the spins tend to align in the direction of the magnetic field, which assist the

electrical transport and decreases the ability of charge localization. So the electron jumping needs less energy. Thus, the reason of this decrement in E_a values is reasonable (Khelifi et al., 2012; Bhattacharya et al., 2003; Khelifi et al., 2014).

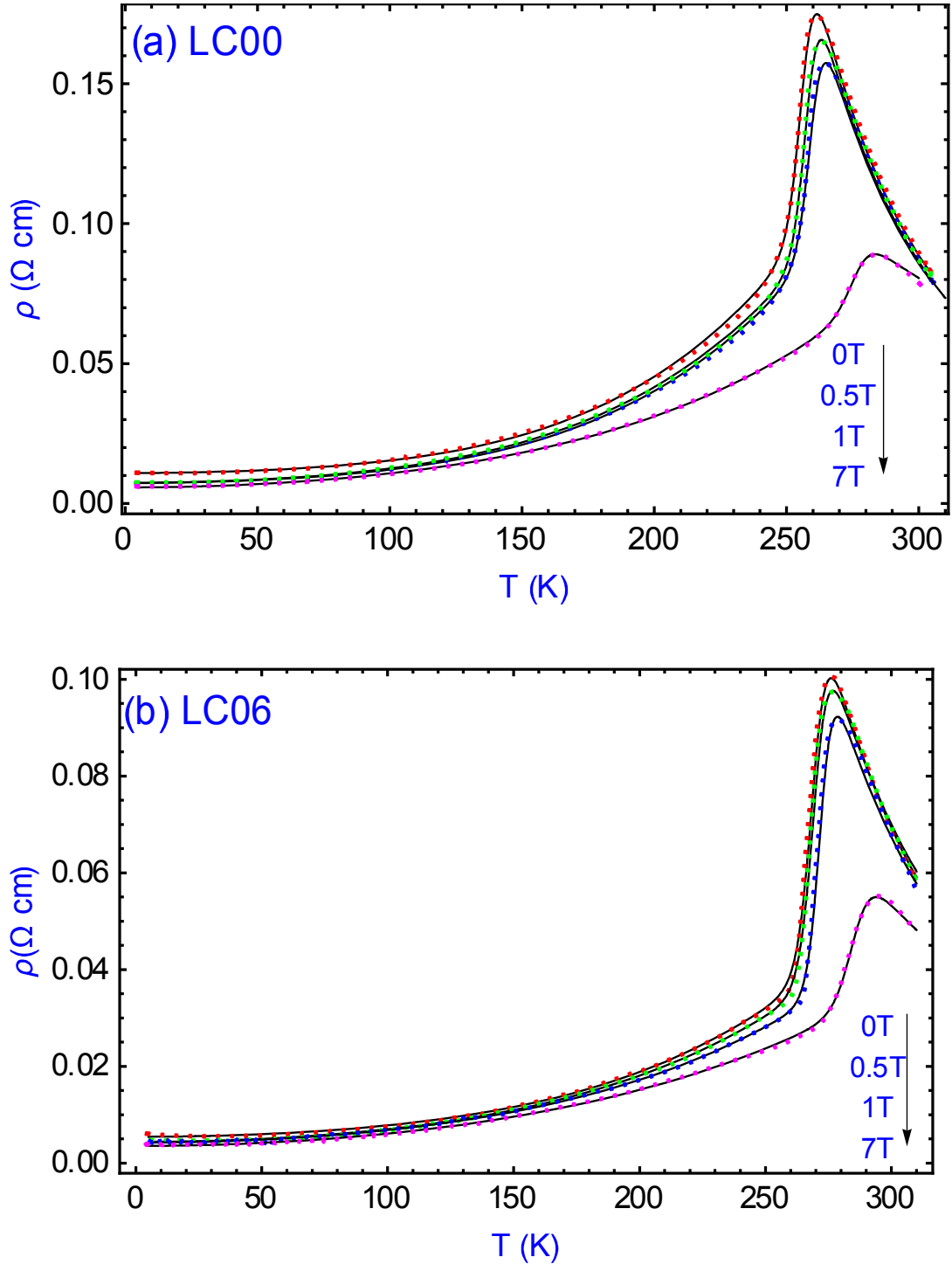


Figure 4.1. Temperature dependence of the electrical resistivity under applied magnetic fields 0, 0.5, 1 and 7 T, respectively for (a) $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, and (b) $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_{0.6}$. The solid lines indicates the best fit to theoretical models.

Table 4.1. Parameters used to fit the experimental data of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ ($x = 0.0, 0.2, 0.4$ and 0.6) compounds in the temperature range 5K and 300K using Eqs. 4.1, 4.2 and 4.3.

LC00	$\rho_0 \times 10^{-2} (\Omega \cdot \text{cm})$	$\rho_2 \times 10^{-7} (\Omega \cdot \text{cm}/\text{K}^2)$	$\rho_{4.5} \times 10^{-13} (\Omega \cdot \text{cm}/\text{K}^{4.5})$
0T	1.089	3.574	8.882
0.5T	0.7396	4.406	7.326
1T	0.7345	4.012	7.419
7T	0.5756	4.726	2.844
	$\rho_a \times 10^{-7} (\Omega \cdot \text{cm})$	$T_c^{\text{mod}} (\text{K})$	$T_{\text{MI}} (\text{K})$
0T	7.612	256.5	261
0.5T	7.117	258.2	262
1T	7.438	260	264
7T	7.550	277	283
	U_0	E_p/k_B	
0T	2.246	1826	
0.5T	2.338	1800	
1T	2.332	1785	
7T	1.891	940.0	
LC06	$\rho_0 \times 10^{-2} (\Omega \cdot \text{cm})$	$\rho_2 \times 10^{-7} (\Omega \cdot \text{cm}/\text{K}^2)$	$\rho_{4.5} \times 10^{-13} (\Omega \cdot \text{cm}/\text{K}^{4.5})$
0T	0.5438	2.147	2.130
0.5T	0.4396	2.443	1.732
1T	0.4245	2.456	1.388
7T	0.3560	2.467	1.063
	$\rho_a \times 10^{-7} (\Omega \cdot \text{cm})$	$T_c^{\text{mod}} (\text{K})$	$T_{\text{MI}} (\text{K})$
0T	6.180	269.0	276.0
0.5T	8.543	270.1	276.6
1T	7.431	272.4	278.0
7T	7.875	286.0	294.0
	U_0	E_p/k_B	
0T	2.305	1774	
0.5T	2.191	1712	
1T	2.555	1682	
7T	1.886	1308	

Fig. 4.2 shows the temperature dependence of the volume fraction of the FM phase f which was obtained from the results of the fitting of the experimental dependence $\rho(T)$ in a zero magnetic field and in a magnetic fields of 0.5, 1 and 7 T. The external magnetic field leads to an increase in the volume fraction of ferromagnetic phase due to an increase in the sizes of the ferromagnetic clusters; i.e., a part of the paramagnetic phase transforms into ferromagnetic conducting regions under the action of the external magnetic field (Gamzatov & Batdalov, 2010). This result in an increase in the conductivity which in turn gives rise to colossal magnetoresistance effect. It can be seen that the volume fraction f is close to unity at a temperature considerably lower than T_{MI} and that, with an increase in the temperature at $T > T_{MI}$, the volume fraction of the ferromagnetic phase approaches to zero.

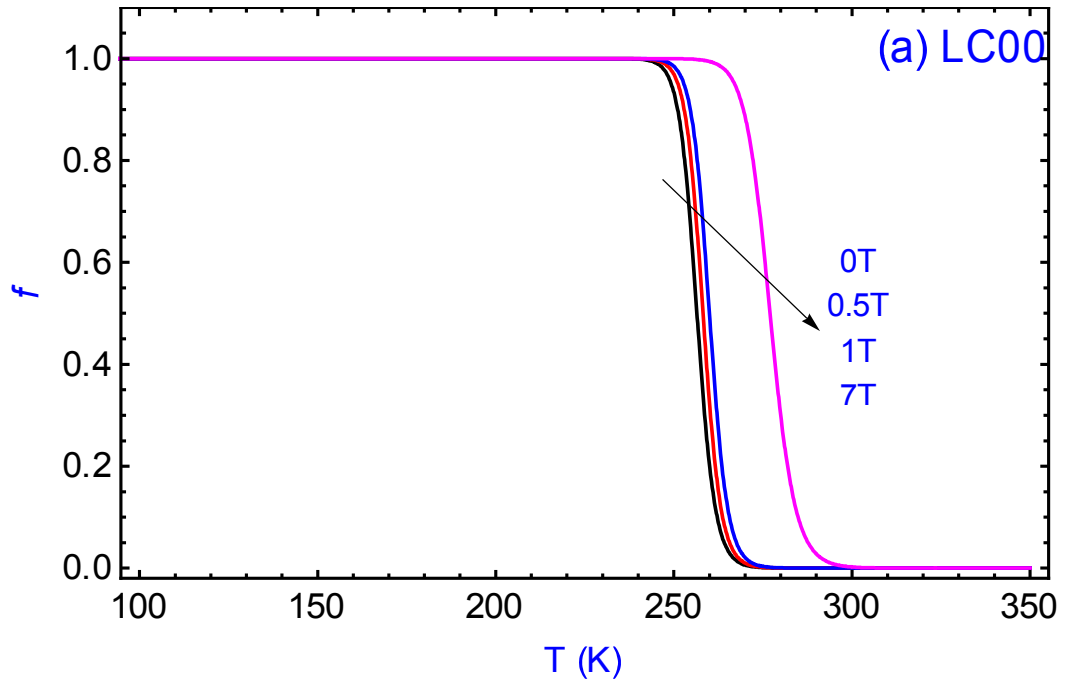


Figure 4.2. The temperature dependence of the volume fractions of the FM, f phases for (a) $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and (b) $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{2.89}\text{F}_{0.6}$ samples using Eqn. 4.3. (*continued*)

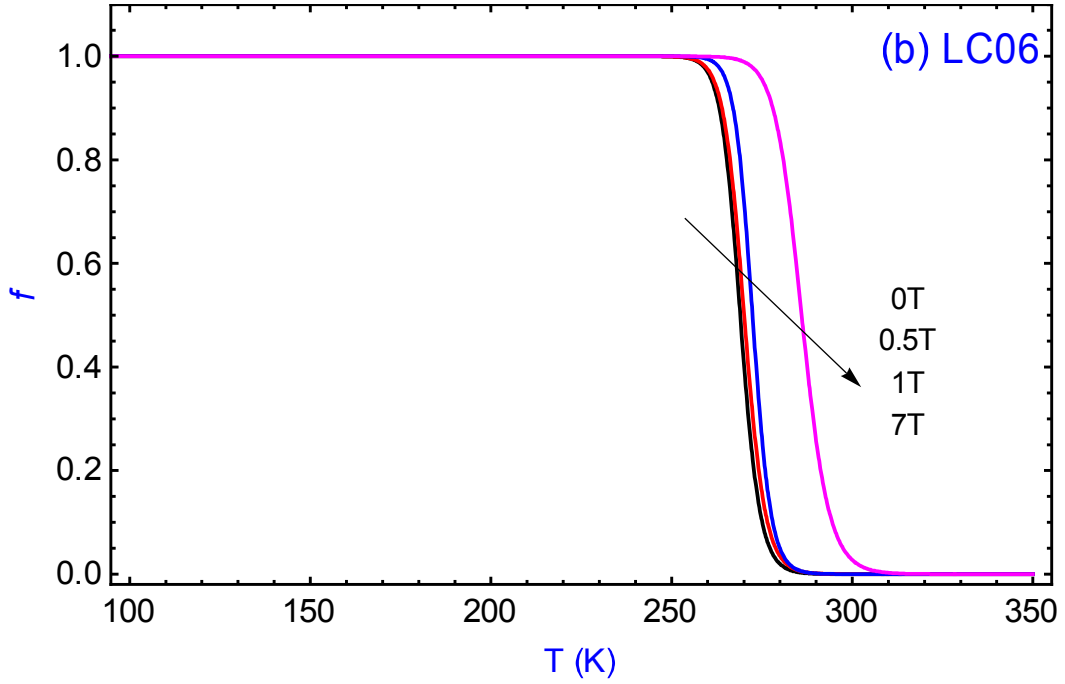


Figure 4.2. The temperature dependence of the volume fractions of the FM, f phases for (a) $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and (b) $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{2.89}\text{F}_{0.6}$ samples using Eqn. 4.3.

It is well known that, the TCR is an important parameter for highly sensitive bolometric applications at room temperature. From the application viewpoint, a high values of TCR indicates high bolometric device efficiency. A larger variation of resistance in the vicinity T_{MI} is a signature of such a property in these samples. The TCR of the LCMO samples was calculated as $(1/\rho)(d\rho/dT)$. The behavior of the TCR as a function of temperature for undoped and doped samples is shown in Fig. 4.3. As can be seen from this figure, there is a disparity seen in the TCR values on both the positive and negative sides of the y-axis and TCR is maximum near T_{MI} and increases with fluorine doping. The maximum values of TCR were $13.29\%K^{-1}$ at 264 K for fluorine doped and $8.75\%K^{-1}$ at 254 K for pure samples. It is obvious that for polycrystalline bulk samples these values are quite reasonable for microbolometer applications. Sudden decrease in the resistivity at T_{MI} results in higher TCR value and sharp insulator to metal transition. The reason for which is due to the presence of highly oriented magnetic spins and strain free structure. Moreover, further optimization of anion substituted hole doped manganites as a thin film can give satisfactory results for application purposes (Awana et al., 2010).

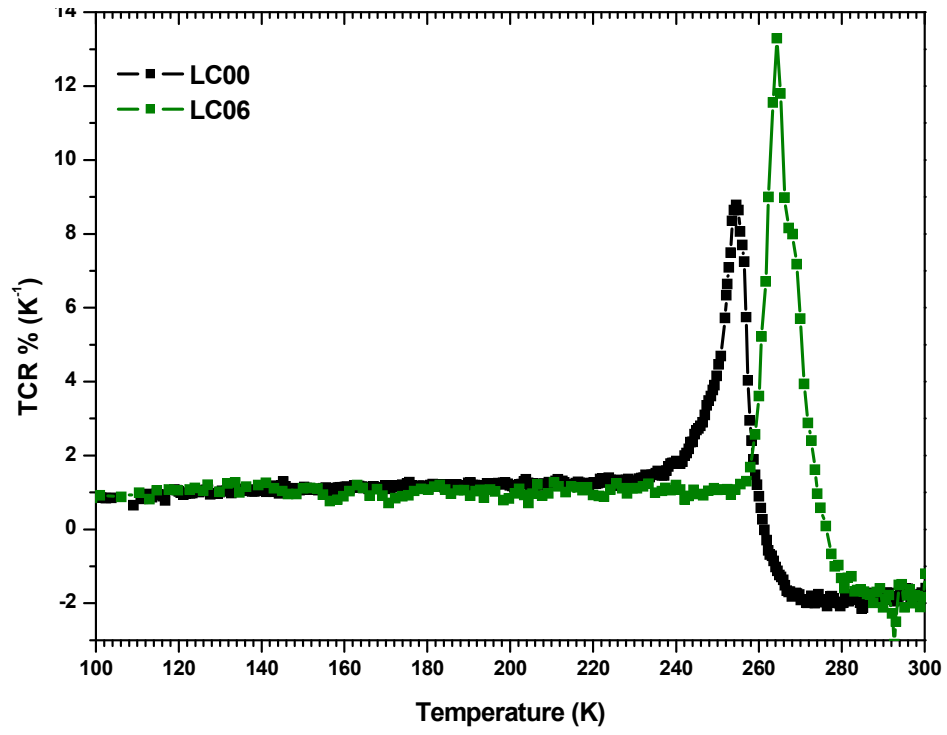


Figure 4.3. Temperature coefficient of resistance (TCR) versus temperature curves of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ ($x=0.0$ and 0.6) compounds.

5. EFFECT OF A-SITE EFFICIENCY/DEFICIENCY IN LCMO SYSTEM

Manganites with perovskite-like structures have been intensively studied for their remarkable magneto-electrical and transport behaviors such as colossal magnetoresistance (CMR) effect, magnetocaloric effect, electroresistance, spin/charge/orbital ordering and so on (Altintas et al., 2012; Han et al., 2011; Liu et al., 2012; Daivajna et al., 2014; Han & Chen, 2010; Mahmud et al., 2013). Due to these fascinating properties, rare-earth manganites have a variety of potential applications in magnetic information storage technology, spin-based devices, magnetic sensors and bolometers (Dyakonov et al., 2009; Liu et al., 2013; Hughes et al., 2010). Among all other interesting properties, the presence of high temperature coefficient of resistance (TCR) nature makes these manganites more outstanding material (Phong et al., 2013). Because, in the case of highly sensitive temperature sensors, significantly large TCR near the room-temperature is a priority criterion.

However, many of these manganites cannot both have a high TCR and CMR value at operating temperature, i.e. at around 300 K. The explanation of the magneto-transport properties of the manganites becomes a big challenge for scientific community. For this reason much efforts has been expanded to understand the conduction mechanism in CMR manganites. Basically, the CMR effect is controlled by two parameters; valency of the dopant and the ratio of ionic radius of dopant to that of rare-earth. Doping manganites with di- or tetravalent alkali- or rare-earth cations leads to mixed valence Mn as Mn^{3+} and Mn^{4+} . A double exchange (DE) mechanism of transport of e_g electron is thought to be the main contributor to the MR effect (Zener, 1951). Difference in the ionic radii distorts the MnO octahedral and modifies MR through Jahn-Teller type interaction (Millis et al., 1995; Millis, 1998). However, recent theoretical and experimental studies have shown that DE and Jahn-Teller effects are not sufficient to explain the physical mechanism of CMR effect (De Teresa et al., 1997; Hwang et al., 1995). Thus different models were established in the aim to understand the multitude mechanisms behind these behaviors. In the low temperature region electron-electron interaction, weak localization effect, electron-

phonon, electron magnon, magnon-magnon correlations are used to explain the resistivity temperature ($\rho(T)$) dependence (Kumar et al., 2010; Gupta et al., 2007; Kondo, 1964). For the high temperature range; the nearest neighbor hopping, the variable range hopping and the nearest small polaron hopping models were used for representing the $\rho(T)$ curves (Coey et al., 1999; Viret et al., 1997; Snyder et al., 1996). In the transition region where a mixture of ferromagnetic (FM) and paramagnetic (PM) behavior is supposed, a percolation model based on phase segregation has been proposed to model the $\rho(T)$ curves (Li et al., 2002, 2007; Narsinga Rao et al., 2009; Khelifi et al., 2012; Yuan et al., 2000, Yuan et al., 2007).

In this chapter of the thesis, my priority aim is to analyze the efficiency/deficiency in A-site hole-doped LCMO system by means of X-ray powder diffraction, electrical resistivity and magnetization measurements. The samples with nominal composition $La_{0.7}Ca_xMnO_{3-\delta}F_{2x}$ ($x = 0.2, 0.3$ and 0.4) were prepared by solid state reaction method as described in Fig. 2.1¹. We will explain directly the electrical transport mechanism of cationic efficient/deficient LCMO system in the framework of a percolation theory. By using this model, the electrical resistivity at any temperature between 5 and 300 K for LCMO system is determined by the change of the volume fraction of ferromagnetic (FM) and paramagnetic (PM) phases which satisfy the Boltzmann distribution (Phong, 2013) as done in chapter 4.

5.1 Structural aspects

The XRD patterns of the samples are shown in Fig. 5.1. The diffraction peaks are indexed in the orthorhombic perovskite structure with the space group Pbnm. Table 5.1 shows the values of cell parameters (a , b and c) and cell volume V . Also, the refinement factors (R_p , R_{wp}) and the goodness of fit (GOF) are given in the same table. The obtained cell parameters are found to close those reported by many groups for lanthanum based manganites. Fig. 5.2 shows the Rietveld refinement for samples with nominal composition of $La_{0.7}Ca_xMnO_{3-\delta}F_{2x}$ with $x = 0.2$ and 0.4 (*One can see Rietveld refinement pattern of $x=0.3$ sample in Fig.3.2(d)*).

¹It should be remarked here that only CaF_2 is used as a source of calcium and fluorine content.

The corresponding Bragg reflection positions are indicated below each pattern. As shown in Table 5.1, the low values of reliability factors represent the good Rietveld refinements. What is worthy to note is that the unit cell volume of the calcium deficient sample is higher than the value of the stoichiometric one. In other words, as oxygen or calcium content increases the unit cell volume decreases due to appearing Mn^{4+} ions which have ionic radius much less than that for Mn^{3+} ($r_{\text{Mn}^{4+}} = 0.64 \text{ \AA}$ and $r_{\text{Mn}^{3+}} = 0.54 \text{ \AA}$) (Shannon, 1976). Thus this increase can be explained by the big vacancy radius due to the Colombian repulsion between cations.

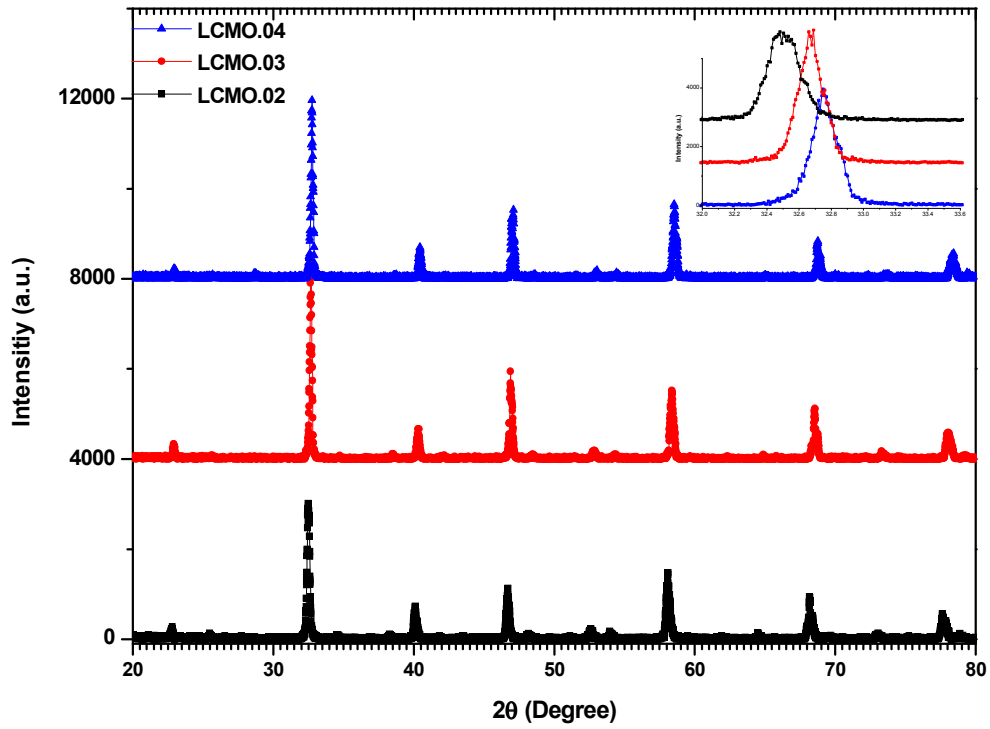


Figure 5.1. X-ray diffraction patterns for powder samples of $\text{La}_{0.7}\text{Ca}_x\text{MnO}_{3-\delta}\text{F}_{2x}$ ($x = 0.0, 0.2$ and 0.3). In the inset we show the width of the peaks with $2\theta = 32.5^\circ$.

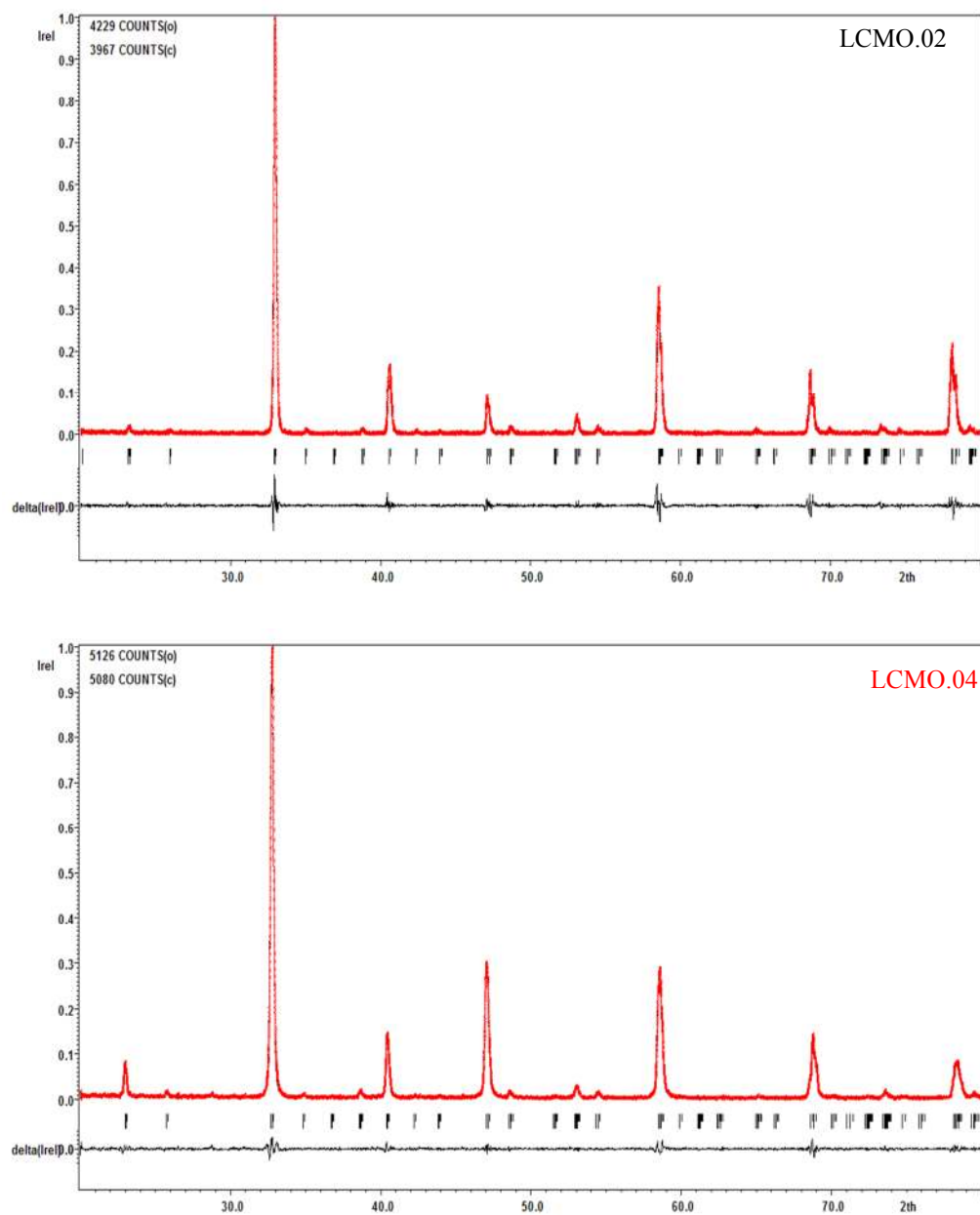


Figure 5.2. Room-temperature X-ray diffraction refinement pattern of $La_{0.7}Ca_xMnO_{3-\delta}F_{2x}$ with $x=0.2$ and 0.4 .

Table 5.1. Rietveld refinement parameters of XRD pattern and the obtained experimental data of $La_{0.7}Ca_xMnO_{3-\delta}F_{2x}$ with $x=0.2, 0.3$ and 0.4 .

Sample	$La_{0.7}Ca_{0.2}MnO_{3-\delta}F_{0.4}$	$La_{0.7}Ca_{0.3}MnO_{3-\delta}F_{0.6}$	$La_{0.7}Ca_{0.4}MnO_{3-\delta}F_{0.8}$
Sample Code	LCMO.02	LCMO.03	LCMO.04
a (Å)	5.4850	5.468	5.4662
b (Å)	5.4792	5.451	5.4499
c (Å)	7.7315	7.745	7.6995
V (Å) ³	232.4	230.9	229.4
δ	0.10	0.11	0.15
R _p , R _{WP}	14.08, 22.79	7.77, 11.7	8.34, 13.94
GOF	1.67	1.04	1.28
Space Group	Pbnm	Pbnm	Pbnm
T _C (K)	186	246	244
T _{MI} (K)	218	276	270

Fig. 5.3 shows the surface morphologies of the samples with 1000× magnification obtained at room. Overall, SEM images show that various sizes of grains are randomly distributed and uniform grain size with significant pores is formed for both samples that one can observe clear grain boundaries. Granular and opened porous nature of all the samples is evident from the SEM pictures. The most notable feature of these images is the decrease in grain-size with increasing calcium content.

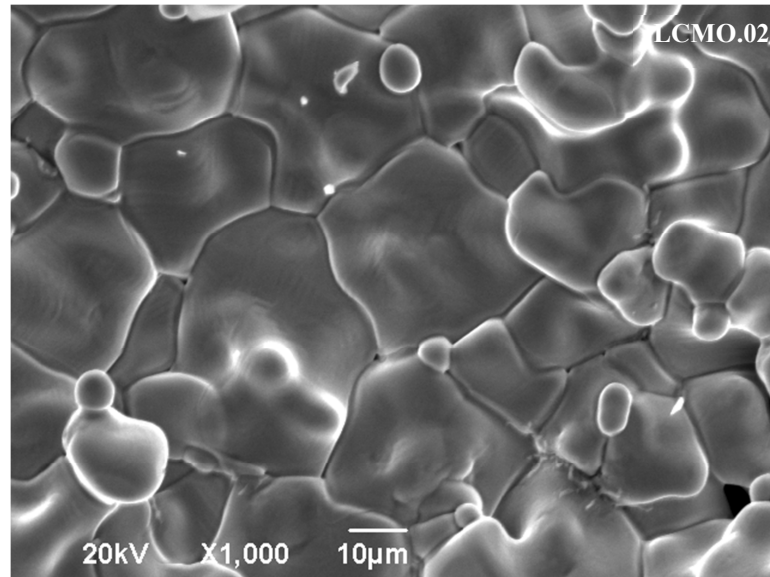


Figure 5.3. SEM micrographs of the $La_{0.7}Ca_xMnO_{3-\delta}F_{2x}$ compounds with ($x=0.2, 0.3$ and 0.4). (continued)

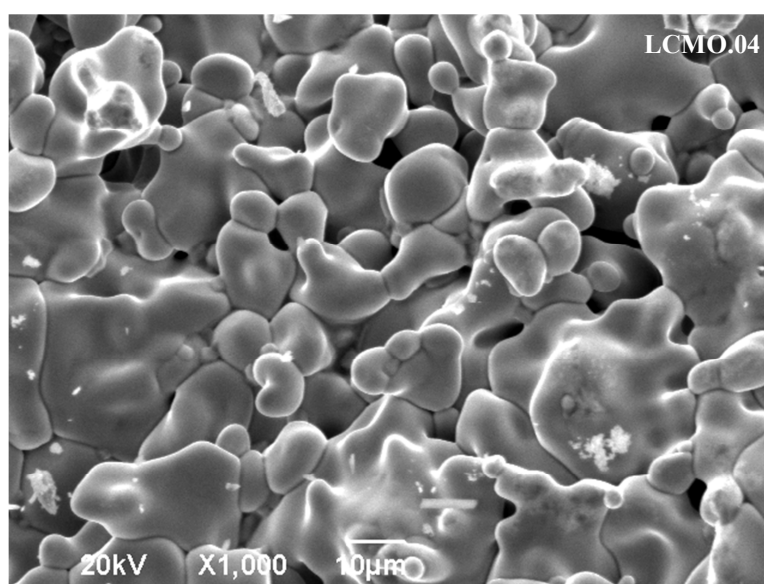
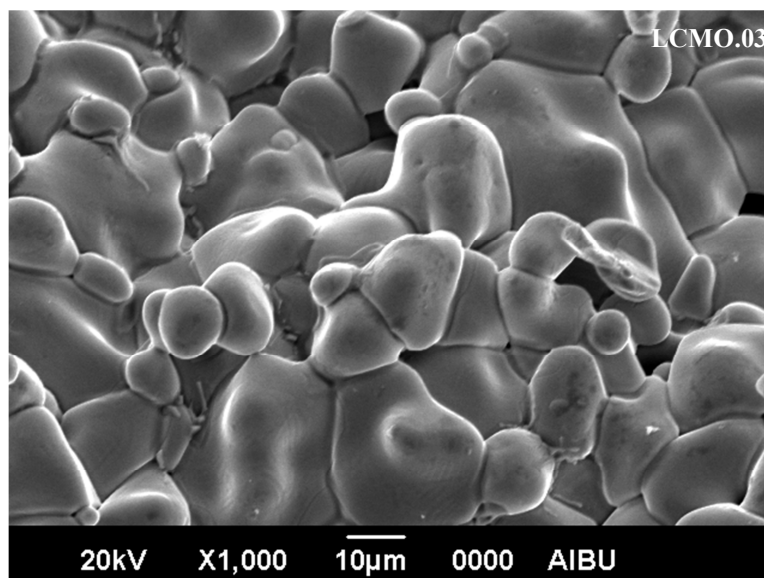


Figure 5.3. SEM micrographs of the $\text{La}_{0.7}\text{Ca}_x\text{MnO}_{3-\delta}\text{F}_{2x}$ compounds with ($x = 0.2, 0.3$ and 0.4).

5.2 Magnetic and electrical behavior

The electrical transport is probably the most attractive physical property of the manganites. The variation of resistance with temperature of the calcium efficient/deficient and optimum doped samples is shown in Fig. 5.4. It is clear that

both samples exhibit a metal-insulator transition. The transition temperature T_{MI} is obtained from the inflection point of $d\rho/dT$ plots. The T_{MI} value which is an extrinsic property that depends on the synthesis conditions and microstructure (Hwang et al., 1995) is given in Table 5.1. A semiconducting behavior (i.e. a negative $d\rho/dT$) is observed in the region above the T_{MI} while a metallic behavior (i.e. a positive $d\rho/dT$) is observed in the region below the T_{MI} . One can see from the same figure that, decreasing calcium content leads T_{MI} to shift gradually to lower temperature (from 269 to 218 K) and the corresponding resistivity peak value ρ_m increases from 0.59 to 6.64 Ω . The variation of T_{MI} and ρ_m with Ca decrement comes from the lattice effect induced by substitution (Det et al., 2008). When Ca with smaller ionic radius substitutes for La in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, the average ionic radius of site A decreases and the Mn-O-Mn bond angle is reduced (Hwang et al., 1995). Thus the hopping process of electrons on Mn sites is changed, which leads to a decrease of T_{MI} and an increase of ρ_m . In addition, the increase of substitution amount strengthens the random potential and Coulomb potential, and then the localization degree of e_g electrons in Mn^{3+} is strengthened, which causes the increase of resistivity (Song et al., 2008).

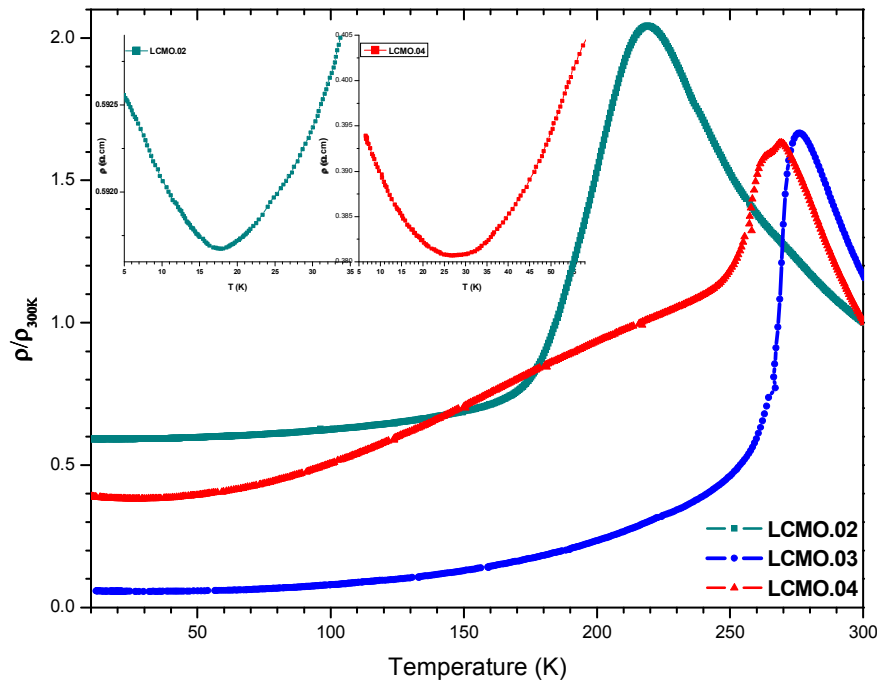


Figure 5.4. Temperature dependence of resistance in zero-applied magnetic field for $\text{La}_{0.7}\text{Ca}_x\text{MnO}_{3-\delta}\text{F}_{2x}$ ($x = 0.2, 0.3$ and 0.4) bulk samples.

In advance of analyzing the experimental temperature dependence of the resistivity in the entire temperature range, let us first investigate $\rho(T)$ at the low

temperatures. For samples $x=0.2$ and 0.4 , it is interesting to see that these samples show a shallow minimum ($T_{\min}$) at about 18 K for LCMO.02 and 28 K for LCMO.04 (see the inset of Fig. 5.4) and on further decrease of temperature below $T_{\min}$, ρ is found to increase which is characteristic feature of an insulator (Jin et al., 1994; Xu et al., 2006). It can be concluded that the resistivity minimum might have originated from the spin dependent scattering (Lalitha & Reddy, 2010; Auslender et al., 2001). In the very low temperature range ($T < T_{\text{upturn}}$), in which the resistivity increases with decrease of temperature, the electron-electron interaction was found to describe well the behavior in the manganites (Kumar et al., 2002). It was also found that weak localization effect with electron-electron interaction can be a cause for the increase of the resistivity with the decrease of temperature (Gupta et al., 2007). Therefore, in order to explain the origin of the low temperature resistivity upturn, the experimental data have been analyzed using the following equation:

$$\rho_{FM}(T) = \rho_0 - \rho_s \ln(T) + \rho_2 T^2 \quad (6.1)$$

where ρ_0 is the residual resistivity contributed of the temperature-independent scattering processes (e.g. : electron-impurity scattering and coulomb interaction), $\rho_s \ln T$ represents the contributions due to Kondo-like spin dependent scattering and $\rho_2 T^2$, which is independent of magnetic field, is attributed to the e-e interaction (Gupta et al., 2007). The experimental resistivity data of LCMO.02 were fitted to Eq. 6.1. For LCMO.03, the ρ - T curve did not show a shallow minimum in resistivity. Thus we have used Eq. 4.1 to fit the temperature dependence of resistivity for sample $x=0.3$. Moreover, to simulate the resistivity vs. temperature curve for sample $x=0.4$, many other models were proposed. We added one more term, two magnon interaction to understand the ρ - T dependence:

$$\rho_{FM}(T) = \rho_0 - \rho_{0.5} \ln(T) + \rho_2 T^2 + \rho_{4.5} T^{4.5} \quad (6.2)$$

In order to simulate and understand the resistivity vs. temperature curves in the high temperature range, $T > T_{MI}$, we have used different models: Mott's 3D variable range hopping (3D VRH) (Mott, 1990), Mott's 2D variable range hopping (2D VRH) (Mott, 1990), Efros-Schklovskii variable range hopping (ES-VRH) (Efros & Shklovskii, 1975), nearest small polaron hopping (SPH) (Emin & Holstein, 1969) and

nearest neighbor hoping (NNH) (Ziese & Srinitiwawong, 1998) models are given by the following equations, respectively:

$$\rho_{PM}(T) = \rho_0 \exp\left(\frac{T_0}{T}\right)^{1/4} \quad (3D \text{ VRH}) \quad (6.3)$$

$$\rho_{PM}(T) = \rho_0 \exp\left(\frac{T_0}{T}\right)^{1/3} \quad (2D \text{ VRH}) \quad (6.4)$$

$$\rho_{PM}(T) = \rho_0 \exp\left(\frac{T_0}{T}\right)^{1/2} \quad (\text{ES-VRH}) \quad (6.5)$$

$$\rho_{PM}(T) = \rho_0 T \exp\left(\frac{E_p}{k_B T}\right) \quad (\text{SPH}) \quad (6.6)$$

$$\rho_{PM}(T) = \rho_0 \exp\left(\frac{E_p}{k_B T}\right) \quad (\text{NNH}) \quad (6.7)$$

where ρ_0 is pre-factor, T_0 represents the characteristic temperature, and $n=1/(d+1)$ depends on dimensionality of the system: for 3-D system, $d=3$, for a 2D-system, $d=2$.

The expression of the Mott's activation energy is given by (Viret et al., 1997):

$$k_B T_0 = \frac{24}{\pi N(E_F) \xi^3} \quad (6.9)$$

Where ξ is localization length, $N(E_F)$ is density of states (DOS) near the Fermi level, k_B the Boltzman constant.

It is found that each of the models cited above can be used to fit the $\rho(T)$ curves. However, according to the values of the coefficient of determination, R^2 , the best one is found with the SPH model. This result is consistent with those works reported in the literature (Ehsani et al., 2012; Gupta et al., 2007; Feng et al., 2005).

Since the combination of residual resistivity, weak localization, electron-electron and electron phonon interactions model is found to be the best way to fit $\rho(T)$ in low temperature range ($T < T_{MI}$), and the nearest SPH is the best model to fit

resistivity curves in the high temperature range ($T_{MI} < T < 300K$), in order to express $\rho(T)$ curves in the entire temperature range we have used them, to express resistivities of the ferromagnetic and paramagnetic regions in the sample, to fit $\rho(T)$ in the entire temperature range by use of the percolation model (Zhu et al., 2002; Li et al., 2007). In such model the resistivity can be written as in Eq. 4.3.

Simulated $\rho(T)$ curves according to the Eq. 4.3 are shown in Fig. 5.5. The fitting parameters are listed in Table 5.2. It is clear from the figure that the closeness of the simulated and experimental $\rho(T)$ curves confirms that the correlation model can be applied to explain the magneto-transport of our experimental data for all temperature range. It also confirms that the electron-electron and electron-phonon scatterings with the weak localization are playing important role in the low temperature transport properties for our samples (Ziese, 2003).

In the insets of Fig. 5.5 we obtained the $f(T)$ curves using Eq. 4.4 and 4.5. It can be seen at low temperature that the FM fraction equal to unity and at high temperature it approaches to zero. This is in agreement with many other experimental observation and theoretical works (Mercone et al., 2005; Perroni et al., 2001).

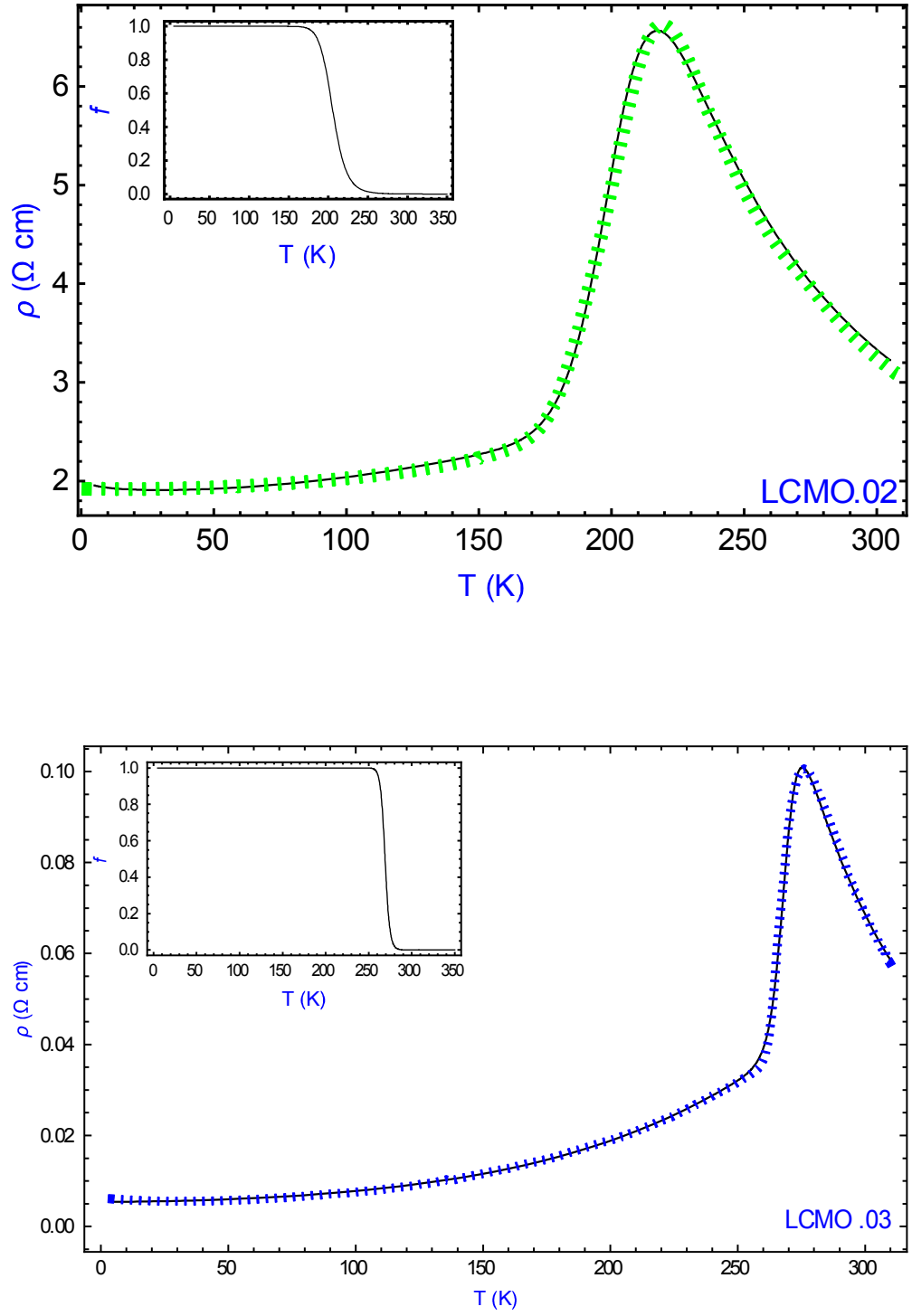


Figure 5.5. Temperature dependence of the electrical resistivity for samples $\text{La}_{0.7}\text{Ca}_x\text{MnO}_{3-\delta}\text{F}_{2x}$ ($x = 0.2, 0.3$ and 0.4). The solid lines indicates the best fit to theoretical models. The insets show the temperature dependence of the volume fractions, f , of the FM phases. (*continued*)

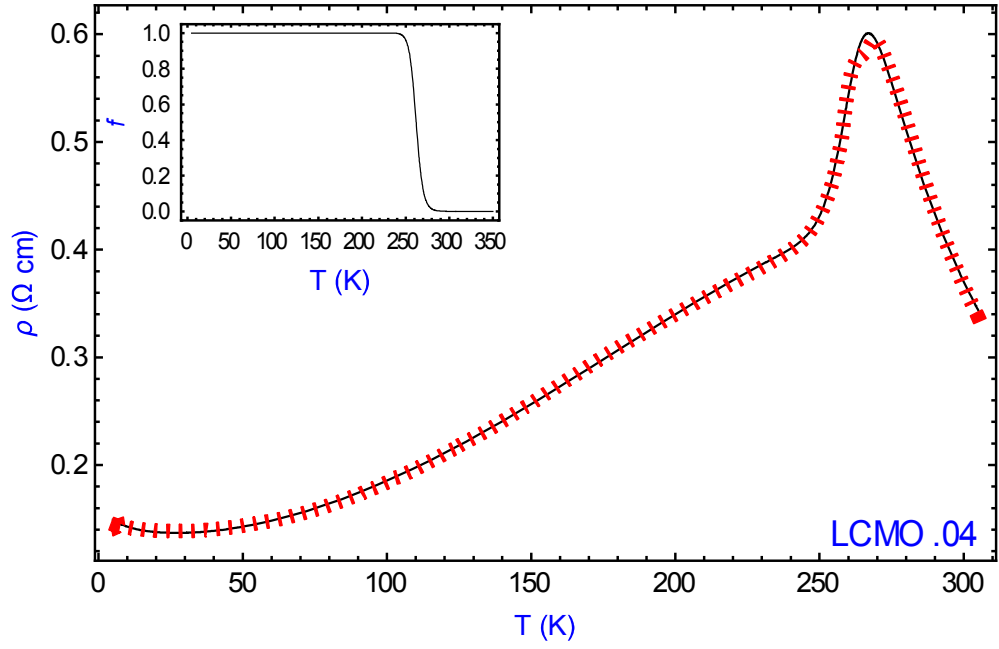


Fig. 5.5. Temperature dependence of the electrical resistivity for samples $\text{La}_{0.7}\text{Ca}_x\text{MnO}_{3-\delta}\text{F}_{2x}$ ($x = 0.2, 0.3$ and 0.4). The solid lines indicates the best fit to theoretical models. The insets show the temperature dependence of the volume fractions, f , of the FM phases.

Table 5.2. Parameters used to fit the experimental data of $\text{La}_{0.7}\text{Ca}_x\text{MnO}_{3-\delta}\text{F}_{2x}$ ($x = 0.2, 0.3$ and 0.4) compounds in the temperature range 5K and 300K using Eqs. 4.3.

	$\rho_0 \times 10^{-2} (\Omega \cdot \text{cm})$	$\rho_2 \times 10^{-6} (\Omega \cdot \text{cm}/\text{K}^2)$	$\rho_s \times 10^{-2} (\Omega \cdot \text{cm})$
LCMO.02	201.2	0.1913	3.518
LCMO.03	0.5438	21.47	-
LCMO.04	16.54	6.889	1.017
	$\rho_{4.5} \times 10^{-12} (\Omega \cdot \text{cm}/\text{K}^{4.5})$	$\rho_a \times 10^{-7} (\Omega \cdot \text{cm})$	U_0
LCMO.02	-	5442	0.4239
LCMO.03	21.30	6.180	2.289
LCMO.04	2.085	50.14	1.506
	$T_c^{\text{mod}} (\text{K})$	$T_{\text{MI}} (\text{K})$	E_p/k_B
LCMO.02	205.5	218	905
LCMO.03	269	276	1774
LCMO.04	262	269	1652

The temperature dependence of ac susceptibility (T) which is measured under an applied field of 1 mT are plotted in Fig. 5.6. All the compositions show the expected phase transition from paramagnetic to ferromagnetic phase when decreasing temperature. The inflection point of ac susceptibility versus temperature curve (see insets of Fig. 5.6) indicates the Curie temperature, i.e. the T_C of all samples were obtained from the peak of $d\chi/dT$ curves. As a result, we note clearly that the magnetization decreases with calcium deficiency due to the decrease of high spin Mn^{3+} concentration and the increase of the low spin Mn^{4+} ions concentration according to the $La_{0.7}^{3+}Ca_{0.3}^{2+}Mn_{0.7-x}^{3+}Mn_x^{4+}O_3^{2-}$ equation. Moreover, T_C values of the stoichiometric and calcium efficient samples remain almost constant, but the T_C value changes marginally for the calcium-deficient sample. According to previous results in the structural part, the reduction of the magnetization of the calcium-deficient sample is explained by the conversion of Mn^{3+} to Mn^{4+} . This conversion leads to the decrease in the magnetization. Besides, the increase of the magnetization for the calcium efficient sample could be explained by the strengthening of the DE mechanism of the ratio (Mn^{3+}/M^{4+}) (Elleuch et al., 2015). Recently, it has been reported that in the case of La/Ca vacancies, some Mn ions might possibly migrate at the A-site resulting an enhance of ferromagnetic state (Orgiani et al., 2010). This explains well the ferromagnetic state in the samples with $x=0.4$.

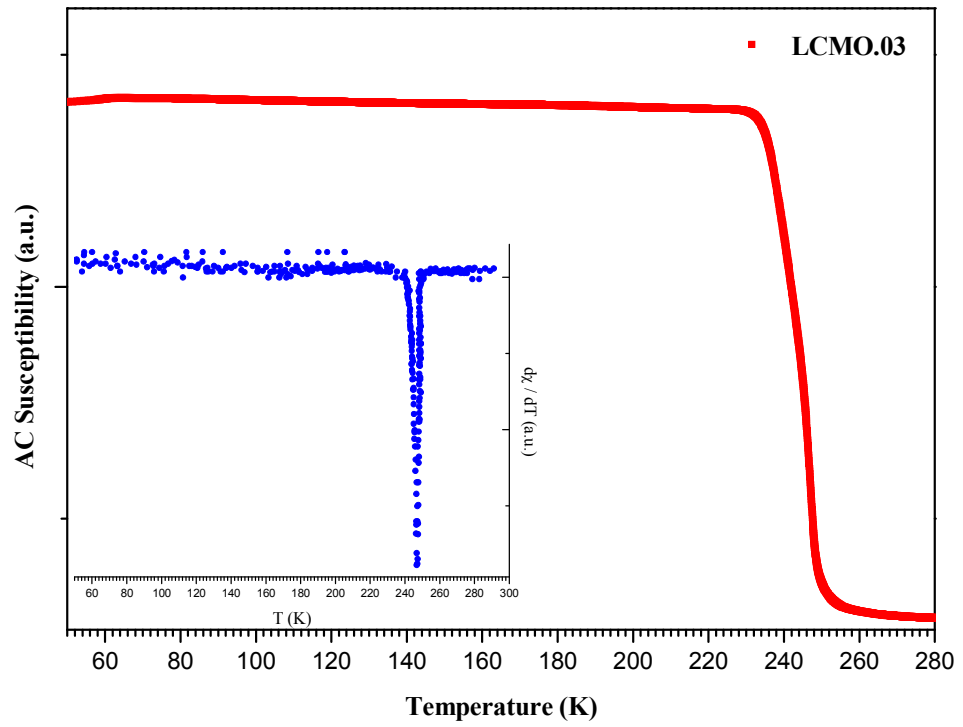
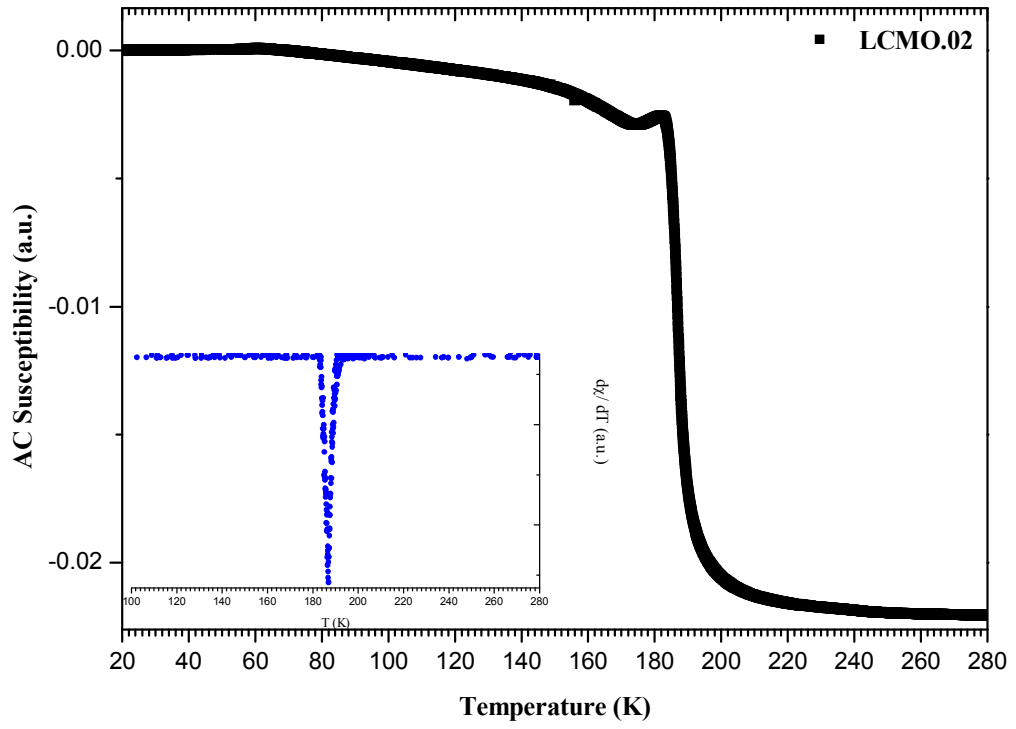


Figure 5.6. Zero-field-cooled ac susceptibility curves measured under applied fields of 1.0 mT at a frequency of 500 Hz for samples $\text{La}_{0.7}\text{Ca}_x\text{MnO}_{3-\delta}\text{F}_{2x}$ ($x = 0.2, 0.3$ and 0.4). (*continued*)

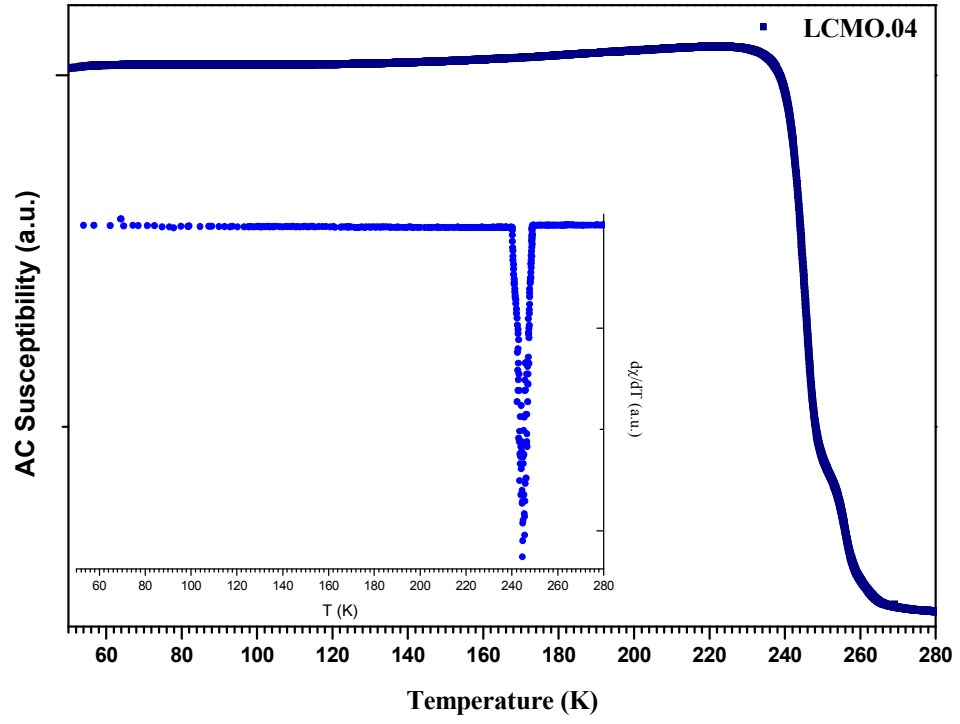


Figure 5.6. Zero-field-cooled ac susceptibility curves measured under applied fields of 1.0 mT at a frequency of 500 Hz for samples $\text{La}_{0.7}\text{Ca}_x\text{MnO}_{3-\delta}\text{F}_{2x}$ ($x = 0.2, 0.3$ and 0.4).

6. CONCLUSION

In summary, this dissertation has focused on a systematic investigation of the anionic and cationic doping at A- and O-site of manganite systems. The studied material system $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ as a member of the class of mixed-valence manganites offers a large variety of structural, magnetic and transport properties. In order to examine the effect of A- and O-site substitution, we have prepared two series of high quality bulk samples by the solid state reaction method. The investigated materials are: $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ with $x = 0.0, 0.2, 0.4$ and 0.6 and $\text{La}_{0.7}\text{Ca}_x\text{MnO}_{3-\delta}\text{F}_{2x}$ with $x=0.2, 0.3$ and 0.4 . We have performed X-ray powder diffraction, electrical resistivity and magnetization measurements to characterize the produced samples.

We have shown that the first series of the form $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}\text{F}_x$ with $x = 0.0, 0.2, 0.4$ and 0.6 are single phased and have the orthorhombic Pbnm space group. The refined lattice parameters were obtained as $a = 5.457 \text{ \AA}$, $b = 5.450 \text{ \AA}$ and $c = 7.697 \text{ \AA}$ for pure sample and $a = 5.468 \text{ \AA}$, $b = 5.451 \text{ \AA}$ and $c = 7.745 \text{ \AA}$ for maximum fluorine doped sample. The cell parameters as well as unit cell volume of the samples are found to increase with fluorine doping. The SEM micrographs reveal that both samples have similar surface topography from the point of view. The grain size of LC00 and LC06 samples are found about $20\mu\text{m}$ and do not depend on the dopant. The electrical and magnetic investigations show that both metal-insulator transition and Curie temperature increase with fluorine doping. The deduced magnetoresistance is slightly higher for the doped sample. The hysteresis in the M-H curve for all samples clearly confirms that we have a ferromagnetic state at low temperatures. It can be clearly seen that both the coercive field and the remanant magnetization is maximum for maximum fluorine doped sample ($x=0.6$). I have also analyzed the temperature dependence of the resistivity of fluorine doped LCMO manganites by using the phenomenological percolation model which is based upon an approach that the system consists of the phase separated ferromagnetic metallic and paramagnetic insulating regions. Under this approximation, the temperature dependence of the volume fraction distribution is supposed to follow the Boltzmann distribution of a two energy-level system, then we used a simple model to describe the PI-FM

transition and CMR. I further show that fluorine doping is an effective way to optimize and enhance temperature coefficient of resistivity (TCR) values in LCMO system. Higher TCR of the present fluorine doped LCMO system could be very useful for infrared/bolometric detector applications.

The second series of the form $\text{La}_{0.7}\text{Ca}_x\text{MnO}_{3-\delta}\text{F}_{2x}$ with $x=0.2, 0.3$ and 0.4 are single phased and crystallize in the orthorhombic structure with Pbnm space group. We can notice that Ca-vacancy leads to an increase of the unit cell volume. SEM images show that various sizes of grains are randomly distributed and uniform grain size with significant pores is formed for both samples that one can observe clear grain boundaries. All our samples exhibit ferromagnetic to paramagnetic phase transition. According to electrical and magnetic studies, the metal–insulator transition temperature, T_{MI} , and Curie temperature, T_{C} , are found to maximum for stoichiometric sample. Moreover, T_{C} values of the stoichiometric and calcium efficient samples are very close to each other while they change marginally for the calcium-deficient sample. Electrical resistivity data is analyzed using different theoretical models in different temperature regions and the closeness of the simulated and experimental $\rho(T)$ curves confirms that the percolation model can be applied to explain the magneto-transport of our experimental data for all temperature range. It should also be concluded that the temperature dependent electrical resistivity in the high temperature insulating regime is analyzed by means of the well-known adiabatic small polaron hopping model for all samples.

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