Introduction

After the discovery of superconductivity in lanthanum cuprates the perovskite materials have received much interest. The existence of metal-insulator transition (MIT) in lanthanum-based manganites was established in early 1950s [1,2], and was extensively studied thereafter. This phenomenon has been observed in a family of doped manganites with perovskite structure of chemical formula $R_{1-x}A_x MnO_3$ (where $R$ is a rare earth ion and $A$ is divalent alkaline earth metal ion). The transition is associated with unusual transport properties, including a large value of magnetoresistance in the vicinity of the transition. These materials got intense scientific importance during the past few years in view of possible technological applications e.g. bolometer, magnetic sensors etc. The parent compound is a charge transfer insulator, with Mn$^{3+}$ ions in different layers coupled among themselves antiferromagnetically via superexchange interaction. The Mn$^{3+}$ ions (having electronic configuration $t_{2g}^{3}e_{g}^{1}$) within a layer are coupled ferromagnetically.

The rare earth ion like La in LaMnO$_3$ exists in 3+ state whereas the oxygen has a valency of 2-. This implies that Mn has to exist in 3+ state to preserve the charge neutrality. On doping with divalent element such as Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$ or Pb$^{2+}$ some of the Mn$^{3+}$ ions convert into Mn$^{4+}$ ($t_{2g}^{3}$) state creating holes in the $e_{g}$ band. A Mn$^{3+}$ -O$^{2-}$ -Mn$^{4+}$ network is thus formed. The metal-insulator transition in manganites has been traditionally attributed to the double exchange mechanism [3]. According to Zener in the double exchange model an electron jumps from Mn$^{3+}$ to Mn$^{4+}$ via the oxygen ion, a process giving rise to conductivity in manganites. It is worth mentioning here that the electron jumps only when spins of
Mn$^{3+}$ and Mn$^{4+}$ are in the same direction. The material becomes ferromagnetic with the onset of conductivity. The Mn 3d and oxygen 2p orbitals form an electronically active band. The bandwidth $W$ depends on Mn-O-Mn angle $\theta$ and Mn-O bond distance ($d_{\text{Mn-O}}$). The transition temperature ($T_c$) increases when the bandwidth of the itinerant $e_g$ electron band broadens. The fine tuning of $W$ and $T_c$ can be done by an appropriate selection of the size of the ionic species at the rare earth site. This affects the bond angle $\theta$ but not the bond length $d_{\text{Mn-O}}$ due to the local disorder in the lattice [4]. On the other hand, the application of external hydrostatic pressure can modify both $d_{\text{Mn-O}}$ and $\theta$ [5]. It has been established that on the application of hydrostatic pressure, $d_{\text{Mn-O}}$ is compressed and $\theta$ opens up which enhances the bandwidth.

The decrease in $T_c$ has been observed on variation of oxygen concentration [6] as well as on substitution of heavier isotope of oxygen. Later on it was realized by Millis et al. [7,8] that the effective carrier-spin exchange interaction of the double exchange model is too weak to lead to any significant reduction of the electron bandwidth, and, hence it cannot account for the observed scattering rate or for the localization induced by slowly fluctuating spin configurations. In view of this shortcoming of double exchange model Millis et al. [7,8] suggested that the essential physics of provskite manganites lies in the strong coupling of carriers to the Jahn-Teller lattice distortion. They argued that in the high temperature state the electron phonon coupling constant $\lambda$ is large (so the polarons become the carriers). As the temperature decreases, the growing ferromagnetic order increases the bandwidth and thus decreasing $\lambda$ sufficiently for metallic behaviour to occur below the Curie temperature, $T_c$, in accordance with polaron theory [9]. A giant
isotope effect [10], the sign anomaly of Hall effect, and the Arhenius behaviour of the drift and Hall mobilities [11] over a temperature range from 2T_c to 4T_c confirmed the polaronic nature of carriers in manganites. Polaron hopping transport accounts satisfactorily for resistivity in the paramagnetic phase.

There are a lot of possibilities of technological applications of these materials due to their interesting properties mentioned above. In view of this fact many new experiments are being performed and new materials with similar properties searched for a precise understanding of the origin and the mechanism of these effects. Generally, in manganites Mn exists in three charge states: Mn^{2+}, Mn^{3+} and Mn^{4+} in orthorhombically distorted octahedra with 3d^5, 3d^4 and 3d^3 configurations respectively. The doping of a divalent cation at the rare earth site converts a proportionate amount of Mn^{3+} ions into Mn^{4+}. On the other hand if a tetravalent ion is doped, a proportionate amount of Mn^{3+} ions is likely to be converted into divalent state i.e. Mn^{2+}.

There are a few reports [12-20] on using Ce ion, believed to be in the tetravalent state, for substitution at the rare earth site. This gives the electron doped colossal magnetoresistance materials with Mn in a mixed valence state of Mn^{3+} and Mn^{2+} analogous to electron doped high-T_c superconductor Nd_{2-x}Ce_xCuO_4. Most of these studies are concentrated on La_{1-x}Ce_xMnO_3 (x=0.2 and 0.3). Mandal and Das [14] initiated work on such type of compounds in 1997. They studied transport properties of Ce doped RMnO_3 (R = La, Pr, Nd) manganites. Later on some reports appeared also on thin films [16,20] of La_{0.7}Ce_{0.3}MnO_3 and La_{0.8}Ce_{0.2}MnO_3. But these workers reported a double transition in resistivity versus temperature plot in bulk samples. Initially no reason was
assigned for the same, but subsequent reports pointed out that some amount of CeO$_2$ remains unreacted and La$_{1-x}$Ce$_x$MnO$_3$ is a mixture of La deficient LaMnO$_3$ and CeO$_2$. These workers compared the x-ray diffraction patterns of La$_{0.7}$Ce$_{0.3}$MnO$_3$ and CeO$_2$ and showed that the three most intense peaks of CeO$_2$ are also present in La$_{0.7}$Ce$_{0.3}$MnO$_3$ [18,19], on the basis of which they concluded that La$_{1-x}$Ce$_x$MnO$_3$ could not form in single-phase form under the preparation conditions employed.

In the light of these reports we undertook the synthesis of a series of La$_{1-x}$Ce$_x$MnO$_3$ (x=0.0 to 1.0) to have a detailed study of structural, electronic and magnetotransport behaviour. We have also grown the thin films for a few of these compositions to observe the difference in structural and transport properties in bulk and thin film forms of the same composition. The question has been raised as to whether the double exchange mechanism is still operative when a tetravalent ion instead of a divalent ion is used for the doping, causing an electron doping similar to that in high $T_c$ superconductors, as already stated. If Ce ions in La$_{1-x}$Ce$_x$MnO$_3$ exist in tetravalent state, Mn$^{2+}$ ions could be formed and the electron-like charge carriers would be responsible for the metallic conductivity and ferromagnetism. Therefore, it is essential to know the valence state of Ce and Mn ions to understand the nature of charge carriers and the related physics in La$_{1-x}$Ce$_x$MnO$_3$. We have investigated the valence state of Mn and Ce in La$_{0.7}$Ce$_{0.3}$MnO$_3$ using x-ray absorption study at Mn L$_{3,2}$ & Ce$_{5,4}$ edges. We also performed the x-ray absorption at O-K edge for a comparative study of the hole and the electron doped LaMnO$_3$. 
The term colossal magnetoresistance is used when the value of magnetoresistance is very large. This large value being observed at very high magnetic field and low temperatures, the applicability of these materials is considerably restricted. All attempts to enhance the magnetoresistance in single phase homogeneous manganite compounds at low fields and at room temperature have not been very successful so far. This has shifted the activity in this field to the emphasis on manipulating the composition of manganites to achieve the said objective.

Some earlier work on superlattices [21] involving manganite layers indicates that the incorporation of interfaces, presumably leading to the strain gradients, cause enhancement of magnetoresistance at low fields, though at low temperatures. Several recent studies on polycrystalline thin films of manganite materials seem to reinforce this suggestion. As discussed earlier, hydrostatic pressure produces some sort of strain in the lattice and modifies the electronic and magnetic properties of manganites [5]. The swift heavy ion irradiation (SHI) introduces a type of permanent strain in the lattice and offers a possibility of tailoring the properties. A few studies on hole doped manganites have been made to investigate this effect [22,24]. In one such report on La$_{0.75}$Ca$_{0.25}$MnO$_3$ film the transition temperature ($T_c$) has been found to rise considerably on irradiation with 250 MeV Ag ion beam [25]. The resistivity is also affected and it shows a marked decrease. It was also observed that at lower dose values the lattice releases strain in the thin film thereby increasing transition temperature. However, at higher dose values, defects are generated in the film, affecting remarkable changes in electrical and magnetic properties [22,24]. As of today there is no literature on the influence
of SHI on the physical parameters of electron doped \( \text{La}_{1-x}\text{Ce}_x\text{MnO}_3 \). With an aim to have an improved understanding of these phenomena, we irradiated the thin films of \( \text{La}_{1-x}\text{Ce}_x\text{MnO}_3 \) (\( x=0.3 \) and 0.5) with 200 MeV Au ion beam with different dose values. The XRD and resistivity measurements were done on the irradiated thin films to study the effect of irradiation.

This thesis consists of five chapters.

**Chapter 1** gives a brief account of the historical background of CMR materials and deals with various theoretical models used to interpret their properties.

**Chapter 2** deals with different experimental techniques used for the characterization of samples. These include x-ray diffraction (XRD), x-ray absorption study (XAS), resistivity, magnetoresistance and swift heavy ion irradiation.

**Chapter 3** is devoted to the structural analysis of bulk samples and thin films of \( \text{La}_{1-x}\text{Ce}_x\text{MnO}_3 \) (\( x=0.0 \) to 1.0). A detailed study has been done on how the structure of \( \text{LaMnO}_3 \) changes on doping with Ce up to the end member of the series (\( \text{CeMnO}_3 \)) using powder x-ray diffraction. The electronic structure studies have been made using x-ray absorption measurement at O-K, Mn-L, and Ce-M edges. Effects of irradiation on the structural aspect have been also discussed in this chapter.

**Chapter 4** consists of results on electronic and magneto-transport of bulk samples. The resistivity versus temperature plots of \( \text{La}_{1-x}\text{Ce}_x\text{MnO}_3 \) (\( x = 0.2, 0.3, 0.5 \)) exhibit a single peak metal-insulator transition. This is contrary to the
observations of other workers on this system, where they reported a double peak transition and associated the second peak with impurity phase. We also observe a higher transition temperature as compared to that reported by earlier workers. These samples also show magnetic transition from antiferromagnetic to ferromagnetic state on cooling. The value of magneto-resistance measured in a low field of 0.2T is found to increase with decrease in temperature and it reaches to more than 20% at the lowest temperature of measurement. On irradiating the thin film of La$_{0.7}$Ce$_{0.3}$MnO$_3$ with swift heavy ion beam, we observe increase in transition temperature and a decrease in resistivity at moderately low fluence values. But at higher fluence values the transition temperature is found to decrease with overall increase in resistivity and the temperature dependence of resistivity plot indicates to the multiphase formation.

In Chapter 5 we summarize our experimental results and analysis. On the basis of these results we conclude that Ce doped LaMnO$_3$ can be formed in single phase if suitable conditions are applied during the synthesis. Ce exists in an intermediate valence state of 3+ and 4+ in Ce doped LaMnO$_3$. Our results of powder x-ray diffraction and temperature dependence of resistivity performed on irradiated samples suggest that the swift heavy ion irradiation can be used as a productive technique to modify the structural and electronic transport properties of manganites.
References


