Chapter 6

Summary and Conclusions

6.1 Introduction

The discovery of colossal magnetoresistance in RMnO$_3$ type manganese pervoskite materials, where R represents rare-earth ion, has evoked enormous interest in these compounds for their potential applications and for the physics involved in the intricate relationship between their structural, transport and magnetic properties. Physical properties of CMR materials primarily depend upon the parent material, amount of doping at R and Mn sites, doping element(s) and synthesis technique used to prepare the material. PMI to FMM transition in these materials is generally explained on the basis DE model proposed by Zener and JT polaronic transport proposed by Millis. However, the study of the CMR materials is found to be much more complex. For example, in many CMR materials ferromagnetic state arises not from DE interactions, but from superexchange
interactions. Still, there is no agreement on common theoretical model which can explain all properties of these materials. Extensive research work on these materials in the last 10 years has opened even more frontiers for research in this field like charge ordering, charged stripes, magnetic phase separation and site-disorder. In the present work, we have made an attempt to contribute to the understanding of the properties of the CMR materials. We have undertaken the detailed experimental investigations of the following two systems.

- **Series I**: site-disordered \( \text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3 \) (\( 0 \leq x \leq 0.20 \)) system which exhibits enhanced \( T_C \) in \( x = 0.10 \) and \( x = 0.20 \) samples.

- **Series II**: \( \text{Sm}_{0.5-x}\text{Pr}_x\text{Sr}_{0.5}\text{MnO}_3 \) system with \( x = 0.0, 0.3 \) and 0.5 in which low temperature ground states are FMM for \( x = 0.0 \), CE-type AFI and charge-ordered for \( x = 0.3 \) and orbitally ordered AFI for \( x = 0.5 \).

We have probed the role of Ti ions in introducing site-disorder, nature of the site-disorder and its effect on structural, transport and magnetic properties of the compounds in series I and studied the effect of local structural changes of \( \text{MnO}_6 \) octahedra on low-temperature ground states of the compounds in series II.
6.2 Site-disordered $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ System.

It is well known that Ti doping at Mn site in $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ compounds, where R is a rare-earth ion and A is an alkaline earth ion, suppresses the DE interaction within $\text{Mn}^{4+}$-$\text{O}$-$\text{Mn}^{3+}$ pairs which leads to decreasing $T_C$ for increasing doping content. It has been shown that in Ti doped manganites Ti is in tetravalent state and occupies $\text{Mn}^{4+}$ sites alone due to their isovalency. However, the synthesis technique plays important part in deciding the properties of these materials and it is possible to synthesize Ti doped compounds wherein Ti$^{4+}$ ions can also occupy $\text{Mn}^{3+}$ sites in the material. On the basis of size considerations, there is a distinct possibility of such a substitution, ionic radius of Ti$^{4+}$ ion being much closer to the ionic radius of $\text{Mn}^{3+}$ ion compared to that of $\text{Mn}^{4+}$ ion. The effect of such site-disorder will manifest in structural, transport and magnetic properties of the compounds.

We have synthesised such site disordered (SD) materials by using low annealing temperature in the solid state reaction method. The samples were characterised by X-ray diffraction, iodometric titrations, four-probe resistivity, MR and a.c as well as d.c. susceptibility measurements. They were further probed by IR, XPS, EXAFS spectroscopic measurements. A site-ordered sample with $x = 0.10$ was prepared again with higher annealing
temperature to understand the effect of site-disorder in SD materials. It was characterised by X-ray diffraction, four-probe resistivity and d.c susceptibility measurements.

Results of resistivity and a.c susceptibility measurements show that samples with $0.00 \leq x \leq 0.05$ exhibit PMI to FMM transition with gradually decreasing $T_C$. However, for $x = 0.10$ and $0.20$, there is no MI transition and $T_C$ increases to R.T. The samples are ferromagnetic and insulating below R.T., over the entire temperature range investigated. To understand these effects, Mn$^{3+}$ and Mn$^{4+}$ contents in the samples were determined using iodometric titrations and XPS measurements. Mn$^{3+}$ content is found to be decreasing with the doping content and Mn$^{4+}$ content is greater than that expected for Ti$^{4+}$ ions occupying Mn$^{4+}$ sites alone. IR spectroscopic investigations reveal that Ti is in tetravalent state in these materials. These two facts led us to believe that a fraction of Ti$^{4+}$ ions occupy Mn$^{3+}$ sites as well. Charge imbalance caused by such a substitution produces cation vacancies in the material to attain the charge balance. Iodometric titrations reveal the presence of cation vacancies, increasing with the Ti doping content. Absence of chemical shift in XPS and XANES spectra and constant lattice parameteres obtained from XRD measurements also support the argument that a fraction of Ti$^{4+}$ ions occupy Mn$^{3+}$ sites. Effect of such a
substitution is also evident through shifting of Mn$^{3+}$-O stretching frequency in IR spectra. Local structures of La and Mn ions, obtained from La and Mn K-edge EXAFS, give nearly constant La-Mn and Mn-Mn bond lengths. This fact can be explained by considering that a part of Ti$^{1+}$ ions occupy Mn$^{3+}$ sites, in addition to the regularly reported Mn$^{4+}$ sites. If Ti$^{4+}$ ions occupy only Mn$^{4+}$ sites, the La-Mn and Mn-Mn bond correlations are expected to increase gradually with doping. Hence, this possibility is ruled out in these materials.

Moreover, a.c. susceptibility measurements show that $x = 0.10$ sample exhibits two ferromagnetic transitions at RT and at about 130 K and MR of the sample is seen to increase substantially between 200 K and 85 K. As MR is expected to be greater at $T_C$ in CMR materials, $T_C$ for this sample can be considered to be 130 K. In that case, $T_C$ at RT must be arising from the site disorder induced by Ti$^{4+}$ ions occupying Mn$^{3+}$ sites. Concentration of DE pairs is reasonably higher in case of such a substitution and the DE pairs are isolated from each other due to the dopant Ti ions and cation vacancies. Hence, high $T_C$ in this sample can be understood in terms of charge transport by variable range hopping polarons that is found to be dominant in higher doped samples. VRH polarons connect such isolated DE pairs and gives rise to weak ferromagnetism and high $T_C$ in this sample.
To conclude, we summarise our work on this series in the following paragraph.

We have been able to synthesize site-disordered La\textsubscript{0.67}Sr\textsubscript{0.33}Mn\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3} (0 \leq x \leq 0.20) samples, identify the nature of the site-disorder and relate its effect to structural, transport and magnetic properties of the compounds. It has been shown for the first time that Ti\textsuperscript{4+} ions can occupy both Mn\textsuperscript{4+} as well as Mn\textsuperscript{3+} sites, in CMR materials. The enhanced $T_C$ in $x \geq 0.10$ samples is due to the VRH polarons which connect isolated DE pairs.

6.3 Sm\textsubscript{0.5-x}Pr\textsubscript{x}Sr\textsubscript{0.5}MnO\textsubscript{3} System.

Compounds of the composition Sm\textsubscript{0.5-x}Pr\textsubscript{x}Sr\textsubscript{0.5}MnO\textsubscript{3} exhibit significantly different low temperature ground states with $x$ and provides an opportunity to understand the causes for attaining such varied ground states. In this series, the end member Sm\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} exhibits paramagnetic insulating (PMI) phase at room temperature (RT) and ferromagnetic metallic (FMM) phase below 95 K. Other end member Pr\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} exhibits PMI phase at room temperature, FMM phase below 255 K and orbitally ordered antiferromagnetic-insulating (AFI) phase below 140 K. However, at
intermediate doping level of $x = 0.3$, Pr$_{0.3}$Sm$_{0.2}$Sr$_{0.5}$MnO$_3$ exhibits CE type charge ordered state below 155 K starting PMI phase at RT to FMM phase below 215 K down to 155 K. Presence of CO state, for the intermediate doping, evokes interest in understanding the role of rare-earth ions in inducing CO ground state.

We have investigated the local structural changes around A-site cation (Pr and Sm) in FMM, PI and CE-type charge-ordered AFI phases of the compound Sm$_{0.2}$Pr$_{0.3}$Sr$_{0.5}$MnO$_3$, PMI and FMM phases of Sm$_{0.5}$Sr$_{0.5}$MnO$_3$ and PMI, FMM and A-type orbitally ordered AFI states of Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ using Pr and Sm K-edge EXAFS.

6.3.1 Pr$_{0.5}$Sr$_{0.5}$MnO$_3$

EXAFS spectra at the Pr K-edge of the sample were recorded at room temperature, 180 K and 50 K so as to study the local structural changes in each of the three phases. The EXAFS spectra at RT and 180 K were fitted in k-space, using one Pr-Mn and three Pr-O correlations obtained from FEFF6.01 for I4/mcm symmetry. Data for 50 K was fitted for Fmmm symmetry with four Pr-O correlations two of which are four coordinated and two are two coordinated. It is shown that the MnO$_6$ octahedra rotate in the ab-plane and tilt away from the vertical along the c-axis when the
sample undergoes FMM to AFI transition. This rotation and tilting of the MnO$_6$ octahedra result in ordering of Mn d$_{x^2-y^2}$ orbitals along the x-axis that is responsible for A-type orbital ordering in Pr$_{0.5}$Sr$_{0.5}$MnO$_3$.

6.3.2 Sm$_{0.2}$Pr$_{0.3}$Sr$_{0.5}$MnO$_3$

EXAFS spectra at the Pr K-edge of the sample were recorded at room temperature, 180 K and 50 K so as to study the local structural changes in each of the three phases. Sm K-edge EXAFS were recorded at room temperature and 50 K. The EXAFS spectra at RT and 180 K were fitted in k-space, using four Pr-O and two Pr-Mn correlations obtained from FEFF6.01 for Pnma symmetry. Data for 50 K was also fitted for Pnma symmetry with six Pr-O correlations with co-ordination number two each. In charge-ordered state, the neighboring MnO$_6$ octahedra rotate about b-axis in opposite directions from their R.T. positions. Changes in Pr-O distances along a-axis can be understood in terms of tilting of MnO$_6$ octahedra. At room temperature, oxygen ions in Mn-O-Mn chain along b-axis are slightly off-axis resulting in Mn-O-Mn bond angle of 174°. In CO state, this Mn-O-Mn angle decreases further due to tilting of the octahedra away from b-axis. Decreasing Mn-O-Mn angle is expected to weaken the double exchange interaction. Shifting of Mn and/or rare-earth ions along c-axis also contributes to the changes.
Pr-O bonds along c-axis. The combined effect, of rotation and tilting of MnO₆ octahedra and the shifting of cations, localises the itinerant e₉ electron and manifests in the charge ordered state. Tilting and rotation of the MnO₆ octahedra reduce the Mn-O-Mn angle, thereby decreasing the FM DE transfer within Mn-O-Mn chains and shifting of the RE cations reduces the carrier charge density in Mn-O-Mn chains. Antiferromagnetic phase arises due to the strengthening of the AF superexchange interactions between the t₂g electrons, in the background of the reduced FM interactions. Results of Sm K-edge EXAFS closely match with those of Pr K-edge EXAFS studies.

6.3.3 Sm₀.₅Sr₀.₅MnO₃

EXAFS spectra at the Sm K-edge of the sample were recorded at room temperature and 50 K so as to study the local structural changes in PMI and FMM phases. The EXAFS spectra at R.T. and 50 K were fitted in back transformed k-space for Pnma symmetry, using four Sm-O correlations with co-ordination number three each and two Sm-Mn correlations with co-ordination numbers two and six respectively.

It is found that slight bending of oxygen in Mn-O-Mn chain is responsible for changes observed in Sm-O correlations at 50 K. The increased Mn-O-Mn angle and reduced spin-disorder at lower temperatures is responsible for
strengthening of FM interactions observed at low temperatures. Straightening of Mn-O-Mn bond angle allows greater overlap of Mn(3d) and O(2p) orbitals and strengthens ferromagnetic coupling between double-exchange pairs.

6.4 Suggestions for Further Work

Research in CMR materials in the beginning of the last decade was focussed on studying different materials with wide variety of A and B site doping, for their structural, transport and magnetic properties. Zener's double exchange theory and JT static and dynamic polaron models proposed by Millis could explain basic physics of CMR properties. However, extensive research in the last 10 years has shown that physics of CMR properties is much more complex. Discoveries like charge/orbital order, magnetic phase separation and site disorders of various types in these materials, have added more degrees of freedom to the studies on CMR materials. With potential applications of CMR materials in magnetic sensors, magnetic storage devices, solid state fuel cells and other smart devices like MEMS, there is a need to identify new materials which exhibit suitable $T_c$, high MR and have other allied properties that are necessary for using these materials in commercial applications. This requires in-depth knowledge of the various
synthesis techniques that can be used to prepare these samples. It is commonly observed that a material prepared by different synthesis procedures have dissimilar structural, transport and magnetic properties. Effect of oxygen partial pressure, annealing temperature and grinding have been studied for some CMR materials. However, although it is known that properties of CMR materials are decided by the synthesis procedure used, there is no enough research work on disorder that is induced in the material by the synthesis procedure used. For example, a few reports have shown that A cation occupies B-site and vice versa in some CMR materials. Moreover, there are diverging views on percentage of cation vacancies on A and B sites in cation deficient samples. Some studies on cation deficient LaMnO$_3$ samples report that cation vacancies are predominantly on A-site whereas some other studies suggest that vacancies are equally distributed on both A and B sites. As cation deficient LaMnO$_3$ samples are used as electrodes in solid state fuel cells, there is a large scope for research on site-disorder in such materials. It has become essential to look for the microscopic properties of the materials to understand their macroscopic properties.

In the present work, we have shown that Ti$^{4+}$ ion can occupy Mn$^{3+}$ as well as Mn$^{4+}$ sites in La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Ti$_x$O$_3$ by controlling the annealing temperature. This adds another degree of freedom to the study on CMR
materials wherein it was reported earlier that $\text{Ti}^{4+}$ ion can occupy $\text{Mn}^{4+}$ sites alone. It will be a good endeavour to identify and investigate other systems wherein such type of substitution takes place.