Preface

Oxide materials have a wide range of property covering from insulators to high temperature superconductors and from ferroelectric to ferromagnetic materials. They possess an enormous range of electrical optical and magnetic properties and thus have great potential for the application of novel device. Perovskite oxides have been subject to various crystallographic, magnetic and electronic investigations due to their wide variety of physical properties. Lanthanoid cobaltites form an important class of perovskite oxide. Among them La$_{1-x}$Sr$_x$CoO$_3$ has been subjected to immense research because of the peculiar way their magnetic and transport properties change with temperature.

La$_{1-x}$Sr$_x$CoO$_3$ is obtained from LaCoO$_3$ by substitution of Sr$^{2+}$ for La$^{3+}$. Strontium substitution brings about remarkable changes in the structural and transport properties of the system. LaCoO$_3$ belong to ABO$_3$ perovskite with rhombohedral distortion. The rhombohedral distortion decreases with increasing Sr$^{2+}$ content and at about 50 % Sr$^{2+}$ content the system is cubic. For Sr$^{2+}$ content $x > 0.5$ the system is tetragonal. The charge compensation for Sr$^{2+}$ substitution for La$^{3+}$ is accomplished either by the oxidation of Co$^{3+}$ to Co$^{4+}$ or by the creation of oxygen vacancy. As the Sr$^{2+}$ content increases, the Co$^{4+}$ content also increases, increasing the conductivity. When Sr$^{2+}$ content $x = 0.5$, the Co$^{4+}$ content reaches its maximum and with further increase in Sr$^{2+}$ content the structural phase transition occurs with the creation of oxygen vacancy and the conductivity decreases. LaCoO$_3$ show high resistivity and antiferromagnetic exchange interaction. But La$_{1-x}$Sr$_x$CoO$_3$ evolves towards a ferromagnetic state with itinerant electrons as Sr$^{2+}$ content increases. The system shows a spin glass type magnetic behavior for low Sr$^{2+}$ doping ($x < 0.25$) due to inhomogeneous magnetic clusters. For higher Sr$^{2+}$ doping the system shows short range ferromagnetic ordering.
La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSCO) has been used in the field of catalysis, gas sensors, and oxygen penetration membranes and as electrode in oxide fuel cells and ferroelectric memory due to its relatively high electrical and ionic conductivity. LSCO has similar crystal structure as that of the most widely used perovskite ferroelectrics like Pb(ZrTi)$_3$, (Pb,La)(ZrTiO$_3$) and (Ba,Sr)TiO$_3$, and have good chemical stability. Therefore LSCO can serve as electrode as well as growth template layer and protective barrier during device fabrication. The LSCO being a conductive oxide electrode, act as a sink for oxygen vacancies thereby reducing the fatigue. LSCO is also an oxygen ion conductor which makes it useful as a cathode material for fuel cells. LSCO also opens up an interesting option as a candidate for n-MOS gate applications as the work function of LSCO is close to 4.2 eV. The large window of electronic, ionic and catalytic properties of La$_{1-x}$Sr$_x$CoO$_3$ makes it a suitable candidate for gas sensing applications. The conductivity of La$_{0.5}$Sr$_{0.5}$CoO$_3$ thin films can be improved by the partial substitution of Co by Ni. Doping Ni to replace Co ion at B-site can change the electrostatic potential due to their different electron affinities. Therefore La$_{0.8}$Sr$_{0.2}$Co$_{1-x}$Ni$_x$O$_{3-\delta}$ can be used for CO detection at relatively low temperatures.

The main objective of this thesis work is to optimize the growth conditions for obtaining crystalline and conducting La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSCO) and La$_{0.5}$Sr$_{0.5}$Co$_{0.5}$Ni$_{0.5}$O$_3$ (LSCNO) thin films at low processing temperatures. The films are prepared by radio frequency magnetron sputtering under various deposition conditions. The thin films were used as electrodes for the fabrication of ferroelectric capacitors using Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ (BST) and PbZr$_{0.52}$Ti$_{0.48}$O$_3$ (PZT). The structural and transport properties of the La$_{1-x}$Sr$_x$CoO$_3$ and La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$ are also investigated. The characterization of the bulk and the thin films were performed using different tools. A powder X-ray diffractometer was used to analyze the crystalline nature of the material. The transport properties were investigated by measuring the temperature dependence of resistivity using a four probe technique. The magnetoresistance and thermoelectric power were also
used to investigate the transport properties. Atomic force microscope was used to study the surface morphology and thin film roughness. The ferroelectric properties of the capacitors were investigated using RT66A ferroelectric tester.

An overview of the developments in the field of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3$ is briefly presented in Chapter 1. The chapter presents a detailed literature review on the materials. $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ is used as electrode for ferroelectric capacitors and for many other applications. The advantages of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ thin films as a potential candidate over other materials are discussed.

Chapter 2 deals with the various deposition methods and characterization tools employed in the present study. The characterization tools include both characterization of the bulk and the thin films.

Chapter 3 presents the preparation and characterization of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3$ system. $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ has been prepared for varying Sr content and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3$ for varying Ni content, both with $x$ varying from 0.1 to 0.6. The structural evolution of both the compounds with varying Sr and Ni content has been examined. $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ prepared for varying Sr$^{2+}$ content were all single phase. The system could be indexed to rhombohedral distorted perovskite structure, space group $R\bar{3}C$ for all except $x = 0.6$, which had a tetragonal structure. $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3$ had some impurity phase in addition to perovskite $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3$. The transport properties of the system with varying doping concentration of Sr$^{2+}$ and Ni$^{3+}$ have been studied using the temperature dependant measurement of resistivity, magnetoresistance and thermoelectric power. The resistivity data indicated a semiconducting behavior for $x = 0.1$ of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and for $x > 0.1$, the system was metallic. The resistivity was found to decrease with Sr$^{2+}$ content with the $x = 0.5$ having the lowest resistivity. Whereas for $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3$, the system was metallic for
lightly doped samples \( x \leq 0.3 \) and with \( x > 0.3 \) it was insulating. The MR of the \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3 \) indicated a small negative MR for the metallic samples with the peak near the critical temperature. But the semiconducting composition showed a large negative MR at low temperature. In \( \text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3 \) only the metallic compositions showed small negative MR and the insulating compositions showed no MR. The thermoelectric power measurements of both the systems indicated large thermoelectric power for the insulating compositions and the metallic compositions had small positive values.

**Chapter 4** presents the preparation and characterization of LSCO thin films by rf magnetron sputtering. The rf power, the annealing conditions, sputtering gas pressure, oxygen partial pressure and substrate temperature were optimized to obtain crystalline and conducting LSCO thin film. The rf power was optimized to be 150 W and the post deposition annealing condition was optimized as 600 °C in oxygen for one hour. The sputtering gas pressure was optimized to be 0.003 mbar for preparing conducting thin films at room temperature. But oxygen incorporation in the sputtering gas was found to deteriorate the film properties. The films prepared with the minimum oxygen partial pressure were single phase with minimum resistivity. Deposition at elevated substrate temperature enhanced the crystallinity of the films prepared at high sputtering gas pressure. Crystalline and conducting LSCO thin films were obtained at substrate temperature as low as 500 °C.

**Chapter 5** explains the growth and characterizations of LSCNO thin films. The deposition pressure, substrate temperature and Ar:O\(_2\) ratio during rf magnetron sputtering has been optimized to get better conducting perovskite thin films. Oxygen incorporation during sputtering was found to improve the crystallinity and conductivity of the thin films. The substrate temperature could be lowered to 300 °C for obtaining crystalline conducting LSCNO thin film. Crystalline thin films were obtained irrespective of the substrate material at the optimized deposition condition. The films deposited on Pt/TiO\(_2\)/SiO\(_2\)/Si substrates showed
considerable variation in resistivity with deposition conditions and gave the minimum resistivity. The LSCNO thin film deposited on Pt/TiO\textsubscript{2}/SiO\textsubscript{2}/Si substrate have the advantage of lower resistivity of Pt and improved fatigue behavior associated with LSCNO thin film. The atomic force microscopy images of the thin films revealed a smooth surface for the films prepared with oxygen intercalation. An exceptionally smooth surface for the thin films deposited on Si substrates facilitates its use in high quality integrated devices.

Chapter 6 explains the preparation and characterisation of ferroelectric capacitors using LSCO and LSCNO as electrodes. Capacitors were fabricated using BST and PZT as the ferroelectric (FE) material. The capacitors had the following structure viz; Pt/TiO\textsubscript{2}/SiO\textsubscript{2}/Si/LSCO/FE/LSCO and Pt/TiO\textsubscript{2}/SiO\textsubscript{2}/Si/LSCNO/FE/LSCNO. The structural, electrical and ferroelectric properties of the capacitors are studied and the properties are compared with capacitors using conventional electrodes.

Chapter 7 presents the summary and outlook.