CHAPTER 3

Preparation and Characterization of $La_{1-x}Sr_xCoO_3$ and $La_{0.5}Sr_{0.5}Co_{1-x}Ni_xO_3$
La$_{1-x}$Sr$_x$CoO$_3$ and La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$ has been prepared by solid state reaction method. A detailed investigation of the structural and transport properties of these materials has been carried out. The properties were found to vary with the concentration of Sr$^{2+}$ and Ni$^{3+}$ in La$_{1-x}$Sr$_x$CoO$_3$ and La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$ respectively. The observed magnetotransport properties were explained using the cluster model and the phase separation theory. The modified Heiks formula has been used to describe the observed thermoelectric behavior of the system.
3.1. Introduction

The wide spectrum of applications and the interesting properties make perovskite cobalt oxide $La_{1-x}Sr_xCoO_3$ an important candidate for scientific research. $La_{1-x}Sr_xCoO_3$ has potential applications in the field of catalysis, dense ceramic membrane, gas sensors, and as electrodes for oxide fuel cell [1-5]. The chemical and crystallographic compatibility of $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) with ferroelectric materials makes it a suitable electrode for ferroelectric memories [6, 7]. The use of LSCO as a cathode in CO$_2$ lasers is reported to improve its output power and operating life [8]. Recently there have been investigations on the possibility of using $La_{1-x}Sr_xCoO_3$ as a thermoelectric material [9]. It has been reported that the partial substitution of Co by Ni in LSCO thin films decreases the resistivity of LSCO [10]. $La_{0.8}Sr_{0.2}Co_{1-x}Ni_xO_3$ powders and thin films have been used as a potential candidate for CO gas sensors as they exhibited strong oxidation to CO and could efficiently convert CO to CO$_2$ [11].

$La_{1-x}Sr_xCoO_3$ is obtained from LaCoO$_3$ by the partial substitution of Sr$^{2+}$ for La$^{3+}$. Strontium substitution brings remarkable changes in the structural and transport properties and gives a complex phase diagram to the $La_{1-x}Sr_xCoO_3$ system [12, 13]. Even though the hole doping brings about the same changes in the transport and structural properties of the perovskite cobaltites and manganite systems, there are certain fundamental difference between the phase diagram of the two. These differences arise due to the unique properties of the cobaltites viz; the existence of spin state transitions and the presence of magnetic ground state in the doped systems. Since the crystal field splitting energy of the Co d states ($E_g$) and the Hunds rule exchange energy are comparable in cobaltites; there is only a small gap between the $t_{2g}$ and $e_g$ states which contributes to the spin state transitions in the system. For example in the parent compound LaCoO$_3$ where the difference is only 10 meV, $t_{2g}$ electrons can be thermally excited into the high spin $e_g$ state [3-5]. But in manganite systems the Hunds rule
exchange energy is larger than the crystal field splitting energy and the high spin state is stable in the Mn based systems [14]. The strong Hunds rule coupling prevents thermal variation of the spin state. The existence of a spin glass state with short range ferromagnetic ordering for low Sr\textsuperscript{2+} doping can be considered as the magnetic ground state for low doping in cobaltites. With higher Sr\textsuperscript{2+} doping the system evolves towards a ferromagnetic metallic state. But the Mn-based systems shows antiferromagnetic charge ordered insulating phase for low doping. It then evolves into a ferromagnetic insulator and ferromagnetic metal with further doping. These basic differences have renewed interest towards the study of magnetic properties of the cobaltites [15]. Also the structural and electrical properties of these system changes remarkably with Sr\textsuperscript{2+} content. The Seebeck coefficient and the thermal conductivity of the La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} with low Sr\textsuperscript{2+} content was found to be favorable for the use as thermoelectric material [9, 16]. Despite of the reports on the use of La\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{3} system for gas sensing applications there are very few reports on the transport and structural aspect of these systems [10]. Therefore study of the La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} and La\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{3} system is important both scientifically and technologically.

In this chapter a detailed investigation on the preparation and characterization of La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} and La\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{3} system are discussed. La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} system has been prepared for varying Sr\textsuperscript{2+} content and La\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{3} system for varying Ni\textsuperscript{3+} content. The structural evolution of both the system with varying Sr\textsuperscript{2+} and Ni\textsuperscript{3+} content has been examined. The transport properties of the system with varying doping concentration of Sr\textsuperscript{2+} and Ni\textsuperscript{3+} have been studied using the temperature dependant measurement of resistivity, magnetoresistance and thermoelectric power. La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} system is found to evolve from a semiconducting phase into a ferromagnetic metallic state with Sr\textsuperscript{2+} doping. Whereas the La\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{3} system evolves into an insulating phase with Ni\textsuperscript{3+} doping. The magnetotransport and the thermoelectric properties of the system has been explained by considering the Co\textsuperscript{3+} and Co\textsuperscript{4+} ions in the intermediate spin state. A cluster model with short range ferromagnetic ordering
has been considered to explain the evolution of the magnetotransport properties of the system.

3.2. Experimental

The compounds of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0.1 \leq x \leq 0.6$) powder were prepared by solid state reaction from stoichiometric mixtures of $\text{La}_2\text{O}_3$, $\text{SrCO}_3$, and $\text{Co}_3\text{O}_4$. Accurately weighed amounts of the reactants in required proportions were mixed together and were ball milled using $\text{ZrO}_2$ balls in de-ionized water for 24 hours. It was then dried and calcined for 24 hours at $1200^\circ\text{C}$. The compounds of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3$ were also prepared by solid state reaction described above from the stoichiometric mixtures of $\text{La}_2\text{O}_3$, $\text{SrCO}_3$, $\text{Co}_3\text{O}_4$ and $\text{NiO}_3$. Pellets of 10 mm diameter and 1 mm thickness were prepared from these powders. The pellets were then sintered at $1400^\circ\text{C}$ for 12 hours.

The structural characterizations were carried out using a Rigaku X-ray diffractometer with Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å). Resistance and magnetoresistance measurements were carried out by standard four probe method using a home made resistivity insert with Oxford superconducting magnet system. Magnetoresistance (MR) is defined as $[\Delta \rho / \rho = (\rho(H) - \rho(0)) / \rho(0)]$, where $\rho(H)$ and $\rho(0)$ are resistivity in the presence and in the absence of magnetic field respectively. For magnetoresistance measurements magnetic field is applied parallel to current direction. Thermoelectric measurements were done by differential technique down to 4K in a closed cycle refrigerator. In the differential technique the sample is sandwiched between two copper blocks and the temperature gradient (2 K) is maintained across them. Well polished surfaces of copper blocks and the sample facilitate better thermal contact and stability in the signal.
3.3. Results and Discussion

3.3.1 Structural Characterizations

Figure 3.1 shows the powder X-ray diffraction (XRD) pattern of the La$_{0.5}$Sr$_{0.5}$CoO$_3$ along with fitted curve obtained after Reitveld refinement. The analysis gave a good fit and the structure was identified as rhombohedral distorted perovskite structure; space group $R\bar{3}C$. Table 3.1 gives the refined structural parameters. The lattice parameters obtained are in agreement with earlier results [17].

![Figure 3.1: Powder XRD pattern (open circles) of La$_{0.5}$Sr$_{0.5}$CoO$_3$. The solid lines through the data represent a numerical least-square refinement fit in the $R\bar{3}C$ space group. The vertical bars below the diffractogram indicate the position of expected Bragg reflections and the solid lines at the bottom of graph is an intensity difference plot between the observed and the fitted diffraction patterns.](image-url)
Table 3.1 Refined structural parameters of La$_{0.5}$Sr$_{0.5}$CoO$_3$

<table>
<thead>
<tr>
<th>System</th>
<th>Rhombohedral</th>
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<td>Lattice parameters (Å)</td>
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<tr>
<td>c = 13.2353(6)</td>
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The XRD pattern of the La$_{1-x}$Sr$_x$CoO$_3$ powder for varying Sr$^{2+}$ content is given in figure 3.2. The samples with Sr$^{2+}$ content $0.1 \leq x \leq 0.5$ can be indexed to that of rhombohedral distorted perovskite structure; space group $R3C$. But for Sr$^{2+}$ content $x = 0.6$, the crystal structure of the sample is tetragonal.

![XRD pattern of the system La$_{1-x}$Sr$_x$CoO$_3$ for x = 0.1, 0.4, 0.5 and 0.6. The * indicates unidentified peaks](image)

**Figure 3.2.** XRD pattern of the system La$_{1-x}$Sr$_x$CoO$_3$ for $x = 0.1, 0.4, 0.5$ and $0.6$. The * indicates unidentified peaks

The crystal structure of La$_{1-x}$Sr$_x$CoO$_3$ is derived from the ABO$_3$ perovskite LaCoO$_3$. The ideal crystal structure of perovskite type oxide ABO$_3$ have the large ionic-size lanthanide ion (A) occupying the body centered position, the small Co ion (B) occupying the corners of the cube and the oxygen ion (O) occupying the edge centers. LaCoO$_3$ is reported to show a small rhombohedral deviation from cubic form, with $a = 3.82$ Å and $\alpha = 90^\circ 42'$ [18]. Jonker and Van Santen has found that this distortion decreases with increasing Sr$^{2+}$ content
and at about 50% Sr$^{2+}$ the XRD pattern no longer shows a splitting up of lines corresponding to rhombohedral distortion and the system is cubic [19]. When Sr$^{2+}$ ion occupies La$^{3+}$ site, the charge compensation is accomplished by either of the two mechanisms; the oxidation of Co$^{3+}$ ion to Co$^{4+}$ or the formation of O$^{2-}$ vacancy $V_0$ [20]. This can be expressed as

$$Ln_{1-x}Sr_x^{2+}Co_{1+x}^{3+}O_3 \quad \text{for } x \leq 0.5,$$

$$Ln_{1-x}Sr_x^{2+}Co^{3+}O_{3-\frac{x}{2}}V_{0\frac{x}{2}} \quad \text{for } x \geq 0.5.$$  

The XRD results in our case give a rhombohedral distorted structure even for $x = 0.5$ which is similar to the one obtained for Vanita et.al [17]. This system may be considered as a fully oxygenated. A fully oxygenated La$_{1-x}$Sr$_x$CoO$_3$ ($x \leq 0.5$) system at room temperature belongs to the space group $R3C$ [21]. When $x > 0.5$; the oxygen vacancy distorts the perovskite phase and results in the appearance of a phase with a lower coordination number for cobalt. This is probably the cause of the tetragonal structure for $x = 0.6$ [20].

The XRD pattern of the La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$ system with varying Ni content is given in figure 3.3. For all Ni concentrations the system may be indexed to that of rhombohedral distorted perovskite structure; space group $R3C$. The XRD pattern shows the presence of monoclinic LaNiO$_{2.5}$ (JCPDS card No: 87-1216) and orthorhombic La$_{1.6}$Sr$_{0.4}$NiO$_{3.5}$ (JCPDS card No: 85-2379) in addition to perovskite LSCNO (JCPDS card No: 87-1082) for all Ni content. All the d values of the LSCNO perovskite system was shifted by an amount of 0.04 Å$^0$. This shift may be due to the incorporation of Ni atoms at Co sites in perovskite LSCO system [22].
Figure 3.3. XRD pattern of the La0.5Sr0.5Co1-xNi_xO_3 system with varying Ni content. Δ and * indicate peak due to LaNiO_2.5 and La_{1.6}Sr_{0.4}NiO_3.5 respectively.

3.3.2 Transport Properties

The transport properties of the LSCO and LSCNO compounds were studied by the resistivity, magnetoresistance (MR) and thermoelectric power measurements. The temperature dependent resistivity measurement revealed the conductivity mechanism in these compounds. The magnetic field response and the charge carrier responsible for conduction were studied using the MR and thermoelectric power measurements respectively.
i) Resistivity Measurements

\[ p(T) = p_0 \exp\left(\frac{T_0}{T}\right)^n, \]  

where \( n = \frac{1}{2} \) and \( T_0 = \frac{\beta}{kg(\mu)a^3} \),

\( g(\mu) \) is the density of states at the Fermi level, \( a \) the localization radius of the states near the Fermi level, and \( \beta \) a numerical constant. \( p_0 \) is generally of the

Figure 3.4. The temperature dependence of resistivity of the La\(_{1-x}\)Sr\(_x\)CoO\(_3\) for 
\( 0.1 \leq x \leq 0.6 \)

The temperature dependence of resistivity of the La\(_{1-x}\)Sr\(_x\)CoO\(_3\) (0.1 \( \leq x \leq 0.6 \)) is as shown in figure 3.4. For \( x = 0.1 \) a semiconductive behavior is observed. The resistivity of this sample follows the relation

\[ \rho(T) = \rho_0 \exp\left(\frac{T_0}{T}\right)^n, \]  

\( 0.1 \leq x \leq 0.6 \)
order of $\frac{1}{\sigma_{Mott}}$, where $\sigma_{Mott}$ is the Mott minimum conductivity in these samples. The conductivity mechanism of this type is Efros-Shlovski (ES) type hopping, which is variable range hopping (VRH) in the presence of a Coulomb gap in the density of states. A plot of $\ln \rho(T)$ vs $T^{-1/2}$ gives a straight line (figure 3.5) at low temperature, which indicates the ES type hopping conduction mechanism for $x = 0.1$ sample [23]. A slope change is observed for the graph around 100 K. This may be attributed to the spin state transition of the system from a low spin to intermediate spin or high spin state [14, 24]. The argument is justified by the presence of an enhanced thermoelectric power for the $x = 0.1$ sample around 100 K (figure 3.14). The value of $\rho_0$ and $T_0$ for the region below 100 K is $15 \times 10^{-3} \Omega \text{cm}$ and 2015 K respectively, which are physically justifiable.

**Figure 3.5.** $\ln(\rho)$ versus $T^{-1/2}$ plot for the $x = 0.1$ composition of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ showing Efros-Shlovski (ES) type hopping.
The thermally activated spin state transition and the corresponding variation in resistivity in the La$_{1-x}$Sr$_x$CoO$_3$ with $x = 0.1$ can be explained as follows. Sr$^{2+}$ doping into the La$_{1-x}$Sr$_x$CoO$_3$ system creates tetravalent Co ions which are responsible for the ferromagnetism and semiconducting behavior of the system. The system have a cluster type behavior with ferromagnetic clusters containing tetravalent cobalt ions in the high spin (HS) (Co$^{4+}$) and low spin (LS) (Co$^{IV}$) state and a semiconducting intercluster medium containing trivalent cobalt ions in the HS (Co$^{3+}$) and LS (Co$^{III}$) state. It is the spin type of the trivalent cobalt ion in the intercluster medium which determines the charge transport through the cluster. The population of the HS and LS trivalent cobalt ion depends on temperature. For T < 100 K, most of the trivalent cobalt ions go to the low spin state. Therefore the trivalent cobalt ions residing at the boundaries between the ferromagnetic clusters localize the charge carriers causing a large increase in resistivity below 100 K. But as the temperature increases above 100 K, the trivalent cobalt ions become high spin and permit the charge transport through the cluster decreasing the resistivity.

For $x > 0.1$, the behavior of the resistivity in the temperature range indicates a metallic nature (figure 3.4). The value of resistivity is found to decrease with increase of Sr$^{2+}$ content and the minimum resistivity was obtained for Sr$^{2+}$ = 0.5. With further increase in Sr$^{2+}$ content the resistivity was found to increase slightly as shown in the figure. The behavior is quite similar to the results reported earlier [14, 15]. The conductivity mechanism of La$_{1-x}$Sr$_x$CoO$_3$ can be explained using the same argument used to explain the structural evolution with Sr$^{2+}$ doping. As the Sr$^{2+}$ content increases, the Co$^{4+}$ content also increases, which decreases the resistivity. When x is 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 resistivity increases. This explains the slight increase in resistivity for $x = 0.6$ [15, 20, 25].

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A closer examination of the resistivity versus temperature plot of the metallic samples (see e.g. $H = 0$ curves in figure 3.8) shows an upturn in the resistivity behavior below 100 K. But the above explanation of the spin state transition of the Co ions cannot be used to explain this phenomenon. Since for $x \geq 0.2$, the concentration of the metallic ferromagnetic clusters is large enough and it exhibits itself as bulk ferromagnetism and the contribution to the conductivity from the trivalent Co ions residing at the intercluster medium is negligible [12, 14, 26]. Mandal et al. [27] has reported that the rise in resistivity for $T < 100K$ can be due to the presence of oxygen vacancies. But the structural evaluation shows a fully oxygenated one for the compound ruling out this possibility. A similar rise in resistivity below 100 K was observed by Wu et al. [15] and it was attributed to the weak localization of charge carriers at low temperature. Ferromagnetic metals at low temperature are reported to have a $T^2$ dependence.
on resistivity due to the electron scattering from the spin waves [28]. This behavior was investigated by plotting the resistivity as function of $T^2$ for La$_{0.4}$Sr$_{0.6}$CoO$_3$ (figure 3.6). It can be seen that the low temperature rise in the resistivity makes a deviation from the $T^2$ dependence. This rise in resistivity is due to the quantum interference effects and the resistivity in the region below 150 K follows the relation

$$\rho = \rho_0 - A\sqrt{T} + BT^2.$$  \hspace{1cm} (3.4)

It is the $\sqrt{T}$ dependence on resistivity which manifests as the upturn in the resistivity at low temperature. Metallic oxides with disorder usually show this type of behavior [29].

![Figure 3.7. Variation of resistivity with temperature for the La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$ for varying Ni$^{3+}$ content](image)
Figure 3.7 gives the variation of resistivity with temperature for the La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$ system for varying Ni concentration. The samples with low Ni concentration, $0.1 \leq x \leq 0.3$ show a metallic behavior. The resistivity was found to increase with increase in Ni concentration. For Ni concentration $x = 0.4$ the sample is semiconducting and with further increase in Ni concentration the system became insulating. Migiakis et al. [30] has studied the effect of Sr$^{2+}$ substitution on the transport properties of LaNi$_{0.2}$Co$_{0.8}$O$_3$ system. The obtained resistivity of the LSCNO system in the present study is comparable to reported results. The increase in resistivity with Ni substitution in LSCO can be explained as follows. The substitution of Ni was made by using NiO along with other constituent compounds for LSCO. NiO is an antiferromagnetic insulator. The electrical transport in LSCO through the direct contact through the grains is disturbed with the introduction of NiO. With increasing NiO concentration some part of the substituted NiO goes into the grains substituting the Co in the perovskite lattice and the remaining goes to the grain boundaries. If Ni substitutes Co in the perovskite lattice the double exchange mechanism involving Co$^{3+}$ and Co$^{4+}$ ions is disturbed as Ni cannot participate in it. Therefore with the increase of the NiO doping level the resistivity of the LSCNO system increases [22]. An upturn in the resistivity behavior below 50 K similar to that observed in the La$_{1-x}$Sr$_x$CoO$_3$ was also observed for the metallic samples in La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$ due to quantum interference effects.

**ii) Magnetoresistance measurements**

The magneto transport of the La$_{1-x}$Sr$_x$CoO$_3$ and La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$ was found to depend on the concentration of Sr$^{2+}$ and Ni$^{3+}$ respectively. The metallic composition of both the systems showed a small negative magnetoresistance (MR) like a typical ferromagnetic metal. But for the semiconducting composition of the La$_{1-x}$Sr$_x$CoO$_3$ system ($x = 0.1$) a large negative MR at very low temperature was observed. But the semiconducting composition in the
La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$ system does not show any MR even at very low temperature. The MR behavior in the metallic region and semiconducting region of the system had different origin.

(a) Metallic samples

![Graph](image)

**Figure 3.8:** Temperature dependence of resistivity in the presence of zero and 5 T magnetic field for La$_{1-x}$Sr$_x$CoO$_3$ (x = 0.1, 0.4, 0.5 and 0.6)

The variation of resistivity with temperature in zero field as well as in 5 T magnetic field La$_{1-x}$Sr$_x$CoO$_3$ system is given in figure 3.8. Figure 3.9 shows the temperature variation of MR at 5 T magnetic field which is calculated from resistivity curves shown in figure 3.8. The Y axis of figure 3.9 shows negative MR in percentage. The negative MR for the metallic compositions indicates it as a typical ferromagnetic metal [14, 15]. The value of MR is found to increase
with Sr\(^{2+}\) content and the maximum MR in metallic compositions was obtained for \(x = 0.5\) which has lowest resistivity. There is a sharp decrease in resistivity below the ferromagnetic transition temperature \(T_c\). For \(x = 0.4\) and 0.6, MR is slightly lower and shows broad feature around transition temperature as compared to \(x = 0.5\).

![Figure 3.9. Variation of MR% with temperature for La\(_{1-x}\)Sr\(_x\)CoO\(_3\) for varying Sr\(^{2+}\) content. The in field resistivity measurements were taken for a field of 5 T](image)

In the Double exchange theory, the electron or the hole transfer between the neighboring sites depends on the relative angle \(\Delta\theta_j\) of the local \(t_{zz}\) spins [31], i.e.

\[
t_{ij} = t_0 \cos \left( \frac{\Delta\theta_{ij}}{2} \right). \tag{3.5}
\]
In the ferromagnetic state the spins are aligned parallel and spin transfer integral \( t_{ij} \) becomes maximum. Therefore the carrier mobility increases and the resistivity is reduced. The peak in the negative MR is observed around the \( T_c \) of the samples. The external magnetic field aligns the local spin moments of the sample. Maximum magnetization due to the alignment of the spin moments is obtained at the critical temperature of the ferromagnetic material [15, 31]. Therefore there is reduced carrier scattering round the \( T_c \) with magnetic field which causes maximum negative MR around \( T_c \). The \( T_c \) of all the compositions was found to be close to 240 K. But there was no significant shift in the \( T_c \) with \( \text{Sr}^{2+} \) content.

**Figure 3.10.** Variation of resistivity as a function of temperature for zero field and for a field of 5 T for \( \text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3 \) for varying \( \text{Ni}^{3+} \) content
For the La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$ system the substitution of Ni$^{3+}$ was found to enhance the resistivity of the system. Figure 3.10 gives the resistivity as a function of temperature for zero field and for a field of 5 T for La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$ system and the variation of percentage of negative MR as a function of temperature at a field of 5 T is given in figure 3.11. The MR was observed only in the metallic composition of this system. The maximum negative MR was shown for the composition $x = 0.3$. With further increase of the Ni$^{3+}$ content the system becomes semiconducting and the negative MR disappears. The peak of the negative MR was found close to the $T_c$ of the system i.e 200 K.

![Figure 3.11](image)

**Figure 3.11.** Variation of MR% with temperature for La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$ for varying Ni$^{3+}$ content. The in field resistivity measurements were taken for a field of 5 T.

The variation of MR as a function of magnetic field at different temperatures for varying Sr$^{2+}$ content for the La$_{1-x}$Sr$_x$CoO$_3$ ( $x = 0.4, 0.5, 0.6$) is shown in figure 3.12. There was an increase in negative MR with increasing magnetic field for all the temperatures studied. In the ferromagnetic region the negative MR was found to increase more sharply with magnetic field. Generally magnitude of MR in ferromagnetic region shows rapid increase at low field which tends to saturate.
at higher magnetic field. However, in the present case MR shows more or less linear trend at low temperatures. The variation in the MR at low temperature can be due to the inhomogeneous ferromagnetic state in these systems [14]. The maximum variation in MR was obtained at 250 K close to the transition temperature of the samples. In the paramagnetic region (above 250 K) the increase in negative MR was not very sharp where the MR increased to a very small value with the increase of magnetic field. The studies on the magnetization of La$_{1-x}$Sr$_x$CoO$_3$ indicate that the magnetization is proportional to magnetic field in the paramagnetic region. Therefore the MR can be considered to have negative $H^2$ dependence on magnetic field. The magnetic field suppresses the spin fluctuation leading to negative $H^2$ dependence on magnetic field for the MR [32].

![Graph showing MR as a function of magnetic field for the metallic compositions of La$_{1-x}$Sr$_x$CoO$_3$ at different temperatures.](image)

Figure 3.12. MR as a function of magnetic field for the metallic compositions of La$_{1-x}$Sr$_x$CoO$_3$ at different temperatures

Figure 3.13 gives the plot of MR as a function of magnetic field for metallic samples (Ni = 0.1 and 0.3) of the series La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$. The MR behavior is
similar to above metallic system. At 300 K MR follows negative $H^2$ dependence indicating paramagnetic state. This behavior is more evident than the $La_{1-x}Sr_xCoO_3$ samples and its transition temperature are close to 300 K as compared to Ni doped sample. Maximum MR was observed at 200 K which is close to $T_c$ of the samples. At 150 K the MR is found to be complex showing small positive MR at low field which changes sign around 1.5 Tesla. This behavior is similar to $La_{0.5}Sr_{0.5}Co_3$ studied by Mahendiran et al. [14].

Figure 3.13. MR as a function of magnetic field for the metallic compositions of $La_{0.5}Sr_{0.5}Co_{1-x}Ni_xO_3$ at different temperatures
(b) Semiconducting Samples

The figure 3.8 clearly indicates a semiconducting type conductive mechanism for the composition $x = 0.1$ of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system over the whole temperature range studied. The onset of metallicity and ferromagnetism is simultaneous in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system. According to the double exchange model the magneto resistance can be observed around ferromagnetic transition temperature [33]. But figure 3.9 indicates a large negative MR (up to 25 %) at low temperature for the $x = 0.1$ composition which keeps on increasing with decreasing temperature. A similar effect of a large and negative MR in semiconducting compositions with the maximum MR near the spin-glass-like transition temperature was observed by Mahendiran et al. [14]. Wu et al. [15] obtained a low temperature MR value up to 35% for the Sr$^{2+}$ content below $x = 0.15$. The observation of large negative MR in the compositions below the critical doping concentration (ie $x < 0.15$) is interesting. It is the Co$^{3+}$ and Co$^{4+}$ spins which make up the ferromagnetic clusters or the magnetic polarons in the cobaltite system. The spin fluctuations in the system are suppressed by the application of a large magnetic field at low temperature. This increases the hopping conductivity of the system contributing to large negative MR at very low temperatures. But the low temperature negative MR was not observed for the semiconducting composition of the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3$ system. The Ni$^{3+}$ substitution beyond $x = 0.3$ in the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3$ system might have destroyed the inherent ferromagnetic ordering of the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system.

The observed magnetotransport properties of the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3$ system can be explained as follows. Thermally activated spin state transition is a peculiar property of the cobaltite system. The comparable crystal field splitting energy and the Hund’s rule exchange energy contributes to the spin state transitions in the $t_{2g}$ and $e_g$ states of the Co ion of the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system [35]. In $\text{LaCoO}_3$, the Co ion is in the low-spin-state.
(LS) $\text{Co}^{III} (t_{2g}^6, S = 0)$ at low temperature. The energy difference between the LS and high spin (HS); $\text{Co}^{3+} (t_{2g}^4 e_g^2, S = 2)$ is only 0.03 eV [26]. The large crystal field stabilizes the low spin state at low temperature. Thermal excitation can provide a spin transition from the LS to the intermediate spin; (IS: $t_{2g}^5 e_g^1$) around 100 K [26, 35]. Metal-Insulator transition is observed in the $\text{LaCoO}_3$ system with the spin state transition to high spin state above 500 K. $\text{Sr}^{2+}$ substitution creates tetravalent Co ions which can take LS: $\text{Co}^{IV} (t_{2g}^5, S = \frac{1}{2})$, IS $\text{Co}^{4+} (t_{2g}^4 e_g^1$, 

$S = 3/2$) and high spin states $\text{Co}^{4+} (t_{2g}^3 e_g^2, S = 5/2)$. The high spin $\text{Co}^{4+}$ is 1 eV lower in energy than low spin $\text{Co}^{IV}$. Thus $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system contains a mixture of LS $\text{Co}^{III} (t_{2g}^6)$, LS $\text{Co}^{IV} (t_{2g}^5)$, IS $\text{Co}^{3+} (t_{2g}^5 e_g^1)$, IS $\text{Co}^{4+} (t_{2g}^4 e_g^1)$ and some HS $\text{Co}^{3+} (t_{2g}^4 e_g^2)$ and HS $\text{Co}^{4+} (t_{2g}^3 e_g^2)$ depending on the temperature and the $\text{Sr}^{2+}$ content [14]. Another important property of the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system is the short range magnetic ordering or the spin glass state for low $\text{Sr}^{2+}$ doping. With higher $\text{Sr}^{2+}$ content the system evolves to a state of long range ferromagnetic ordering [15].

We have interpreted our results considering a cluster model for the system. The exchange interactions between ions with the same valency state are antiferromagnetic. For low $\text{Sr}^{2+}$ content the Co ion is mostly in the trivalent state and hence the system is dominated by an antiferromagnetic interaction between the trivalent Co ions. As the $\text{Sr}^{2+}$ content increases the fraction of the $\text{Co}^{4+}$ state increases. The exchange interaction of the tetravalent Co ion with the high spin trivalent Co ion is ferromagnetic. Therefore with the increase of the $\text{Sr}^{2+}$ content the system phase separates into ferromagnetically interacting hole-rich clusters in an antiferromagnetically correlated matrix. The onset of ferromagnetic transition takes place at the critical temperature $T_c$. But the ferromagnetic phase does not have a long range order as the cluster of ferromagnetic regions is
embedded in antiferromagnetic matrix [34, 14]. The application of the magnetic field causes a local spin ordering and reduces the resistivity of the system leading to negative MR. This effect is more prominent near the ferromagnetic transition temperature $T_c$ of the system as the field induced magnetization is more near $T_c$. At $x = 0.5$ the Co$^{4+}$ content is maximum which maximizes the strength of the double exchange causing maximum MR [15]. This explains the observed negative MR for the metallic composition of La$_{1-x}$Sr$_x$CoO$_3$. In La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$ the low doping of the Ni$^{3+}$ does not interrupt the ferromagnetic ordering of the La$_{1-x}$Sr$_x$CoO$_3$ system. Therefore the local spin alignment due to the applied magnetic field can be considered as the reason for the negative MR in the metallic composition of La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$. But the maximum negative MR in this system was not observed for the most metallic composition. This can be due to the increased scattering effect of the charge carries which compensates the local ordering due to magnetic field. The new phase separation model can be used to interpret the large MR observed in the semiconducting composition of the La$_{1-x}$Sr$_x$CoO$_3$. According to this model the ferromagnetic grains are embedded in antiferromagnetic matrix. The ferromagnetic phase is metallic with low resistivity whereas the antiferromagnetic phase is insulating with high resistivity. With the application of magnetic field antiferromagnetic phase can be converted into ferromagnetic phase causing large magnetoresistance. This phenomenon is more evident near the percolation limit where the application of the magnetic field leads to colossal magnetoresistance as the ferromagnetic clusters form a percolative path [35, 36]. But in the semiconducting compositions of La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$ the higher Ni$^{3+}$ content disrupts the inherent ferromagnetic ordering of the La$_{1-x}$Sr$_x$CoO$_3$ causing no MR even at very low temperatures [22].
iii) Thermoelectric power measurements

Thermoelectric power is a zero current transport coefficient which can probe intrinsic properties of the material without being affected by defects such as grain boundaries. Thermoelectric power can be used to clarify the electronic structure as it is sensitive to the band structure and carrier mobility near the Fermi level [38, 39].

![Thermoelectric Power vs Temperature](image)

**Figure 3.14.** Variation of thermoelectric power with temperature for varying Sr$^{2+}$ content for \(La_{1-x}Sr_xCoO_3\)

Figure 3.14 shows the variation of thermoelectric power \(S(T)\) with temperature for \(La_{1-x}Sr_xCoO_3\) for varying Sr$^{2+}$ content. The variation of \(S(T)\) with temperature for \(La_{1-x}Sr_xCoO_3\) with \(x = 0.1\) is quite different from that of samples with higher values of \(x\). For \(x = 0.1\) the \(S(T)\) increases with temperature to very
high value of 160 $\mu$V/K at a temperature of 130 K. It remains at this value up to a temperature of about 150 K and thereafter decreases smoothly with temperature. The behavior is quite similar to that observed by Senaris-Rodriguez et al. [12]. For the compositional range $0 < x \leq 0.05$ an increase in thermopower to a very high value was observed, and a plateau was defined with two critical temperatures $T_s$ and $T_s'$, in the S(T) versus temperature curve. But the plateau region is not well defined in the present case. The plateau region in the S(T) versus temperature curve is caused by an electrical conduction dominated by small polaron holes of nearly constant concentration [12].

The high value of thermo electric coefficient for $x = 0.1$ can be explained considering the spin states of the Co ions in the system. In La$_{1-x}$Sr$_x$CoO$_3$ the crystal field splitting energy and the Hunds rule exchange energy of the Co d states are comparable. Therefore the system can undergo thermally activated spin state transitions. In LaCoO$_3$, the trivalent Co ion is in the low-spin-state (LS) Co$^{3+}$ ($t^6_{2g}$, $S = 0$) at low temperature. It can undergo a spin state transition to an intermediate spin state (IS) (Co$^{3+}$: $t^5_{2g}$e$^1_{g}$) at 100 K and to a high spin state Co$^{3+}$ ($t^4_{2g}$e$^2_{g}$, $S = 2$) above 500 K. Sr$^{2+}$ substitution creates tetravalent Co ion which can exist in LS: Co$^{4+}$ ($t^5_{2g}$, $S = 1/2$), IS Co$^{4+}$ ($t^4_{2g}$e$^1_{g}$, $S = 3/2$) and HS Co$^{4+}$ ($t^3_{2g}$e$^2_{g}$, $S = 5/2$) states. The Co ion in La$_{1-x}$Sr$_x$CoO$_3$ with $x = 0.1$ at a temperature around 100 K can be considered to have the identical spin configuration as the parent compound LaCoO$_3$. As the energy difference between the low spin and the intermediate spin states of the trivalent Co ion is only 100 K the system become degenerate at 100 K. This strong degeneracy causes an enhanced thermo power close to 100 K for the $x = 0.1$ system.

Also according to the generalised Heike’s formula, the thermoelectric power is given by
\[ S = -\frac{k_B}{e} \ln \left( \frac{g_3}{g_4} \cdot \frac{x}{1-x} \right) \]  

(3.6)

where \( g_3 \) and \( g_4 \) denote the number of configuration of \( \text{Co}^{3+} \) and \( \text{Co}^{4+} \) ions and \( x \) is the \( \text{Sr}^{2+} \) content [40, 24]. Therefore the ratio of the number of configuration of the Co ions is also crucial in determining thermopower. Koshibae et al. [24] has used the above relation to find out the thermoelectric power of the Co oxides. The calculations show that not only the degeneracy of the Co ion but also the ratio between the spin states of the Co ion i.e. \( \frac{g_3}{g_4} \) is crucial in determining the thermopower of cobalt oxides. The maximum thermopower was obtained for the cobalt oxides when the trivalent Co ion was in the LS state and the tetravalent Co ion was in either LS or in a combination of LS and HS states even though there were other spin configurations for the system which were degenerate. Therefore in \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3 \) with \( x = 0.1 \) beyond 150 K, the spin configuration of the Co ions changes which changes the \( \frac{g_3}{g_4} \) ratio of the system leading to a decrease in thermopower [24, 26].

The inset of the figure 3.14 shows the variation of \( S (T) \) versus temperature for higher \( \text{Sr}^{2+} \) content. The value of \( S (T) \) for \( x > 0.1 \) is very low and it has negative values within the ferromagnetic temperature domain. At higher temperatures it rises to small positive values. The figure shows a bend in the curve at \( T \sim T_c \) and this bend was found to shift towards the high temperature side with the increase of \( x \). It exhibits a minimum with negative value around 100 K and rises to small positive values at room temperature indicating a metallic behavior. But for \( x = 0.6 \) the \( S (T) \) values remained to be negative over the whole temperature range even though it increased beyond the negative peak around 100 K. This negative value of \( S (T) \) may be due to the large FM clusters in the sample. The magnitude of \( S (T) \) at room temperature was found to decrease monotonically with increasing \( \text{Sr}^{2+} \) content. The low value of the thermoelectric power for the \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3 \) with large \( \text{Sr}^{2+} \) content can also be explained using the Heikes
formula. The spin state of the Co ions changes with increasing Sr\(^{2+}\) content and temperature. This changes the \(g_3/g_4\) ratio of the system leading to low thermoelectric power. Even the sign of the thermoelectric power was found to depend on the \(g_3/g_4\) ratio which explains the small negative values of thermoelectric power for the system in the ferromagnetic region. The presence of large ferromagnetic clusters can also contribute to the negative thermoelectric power of the system.

![Graph showing variation of thermoelectric power with temperature for varying Ni\(^{3+}\) content](image)

**Figure 3.15.** Variation of thermoelectric power with temperature for varying Ni\(^{3+}\) content for La\(_{0.5}\)Sr\(_{0.5}\)Co\(_{1-x}\)Ni\(_x\)O\(_3\) in comparison with La\(_{0.5}\)Sr\(_{0.5}\)CoO\(_3\) (S\(_5\) in the figure)

Figure 3.15 shows the variation of thermoelectric power with temperature for varying Ni concentration for La\(_{0.5}\)Sr\(_{0.5}\)Co\(_{1-x}\)Ni\(_x\)O\(_3\) in comparison with the thermoelectric power of La\(_{0.5}\)Sr\(_{0.5}\)CoO\(_3\) (S\(_5\) in the figure). The XRD analyses of
the La\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{3} samples have shown the presence of some impurity phases in addition to perovskite La\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{3}. Fairly high purity of the samples is particularly important for thermo power determination at low temperatures [41]. Therefore the thermoelectric power data of Ni doped samples is considered from 100 K onwards only. For small values of Ni content; Ni = 0.1, the variation is similar to that of La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} with x > 0.1. It has negative values within ferromagnetic temperature domain and rises to very small positive value at higher temperatures. This negative value for the most conductive sample in the La\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{3} system is due to the scattering phenomena which dominate in the system. The reduced negative MR for this particular system further justifies this argument. For x = 0.3 sample the value of S(T) remained negative over the whole temperature range. This can be due to the large ferromagnetic clusters in the sample as the system showed largest negative MR among the compositions studied. For highly Ni doped sample; Ni = 0.5 and 0.6, the S(T) was found to steadily increase with temperature and raised to high value of S(T) indicating an insulating behavior. The temperature dependence of resistivity of highly Ni doped samples also indicated an insulating behavior. Thus the variation of S(T) with temperature for Ni doped samples clearly indicated a metallic behavior for light Ni concentration between 0.1 ≤ x ≤ 0.4 and an insulating behavior for x ≥ 0.5.

3.4. Conclusion

La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} and La\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{3} were prepared by solid state reaction. La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} prepared for varying Sr\textsuperscript{2+} content were all single phase. The system could be indexed to rhombohedral distorted perovskite structure with space group \textit{R}\textsubscript{3}C for all except x = 0.6, which had a tetragonal structure. La\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{3} had some impurity phase in addition to perovskite La\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{1-x}Ni\textsubscript{x}O\textsubscript{3}. The temperature dependent resistivity data of the La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} indicated a metallic conductivity for x > 0.1 and for x = 0.1 the system was semiconducting. The resistivity was found to decrease with Sr\textsuperscript{2+}
content with the \( x = 0.5 \) having the lowest resistivity. The temperature dependant resistivity of the \( \text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3 \) system indicated a metallic behavior for lightly doped samples (\( x \leq 0.3 \)). The sample with \( x = 0.4 \) was semiconducting and with further increase in \( \text{Ni}^{3+} \) the system became insulating. The MR of the \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3 \) indicated a negative MR for the metallic samples with the peak near the critical temperature. The most metallic system (\( x = 0.5 \)) had the maximum MR. For the semiconducting composition \( x = 0.1 \) the MR behavior was different from that of metallic samples and gave 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 the negative MR and the maximum MR was obtained for \( x = 0.3 \). The thermoelectric power measurements of the \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3 \) system gave a large thermo power for the insulating sample (\( x = 0.1 \)) due to the degeneracy of the trivalent and tetravalent Co ions in the system. For metallic compositions the thermoelectric power increased with temperature to a small positive value like a typical ferromagnetic metal. For \( \text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3 \) system the conducting samples (\( x \leq 0.3 \)) gave negative value for the thermoelectric power within the ferromagnetic temperature domain and rose to small positive values at room temperature. The thermoelectric power of the insulating samples of the \( \text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3 \) system rose to high positive values with temperature as in \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3 \) system.
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