Chapter 3

Colossal thermoelectric power in charge ordered lanthanum calcium manganites (La$_{0.5}$Ca$_{0.5}$MnO$_3$)

This chapter deals with the synthesis of Lanthanum calcium manganites (La$_{0.5}$Ca$_{0.5}$MnO$_3$) with a composition close to charge ordering, by high energy ball milling and discusses its thermoelectric power in the temperature range of 5K-300K. Mandal’s model has been applied to fit thermoelectric power data in the region below the Curie temperature (T$_C$). For temperatures lower than 120K, due to the co-existence of a charge ordered state with a spin-glass state, the variation of thermoelectric power is maximum and exhibited a colossal peak value. This has been explained by incorporating Kondo properties of the spin-glass along with magnon scattering. FC-ZFC magnetization measurements indicate the existence of a glassy state in the region corresponding to a maximum value of thermoelectric power. Mott’s polaronic model has been employed to explain the thermoelectric power observed in the high temperature region (T>T$_C$). X-ray Photoelectron Spectroscopy has been utilised to estimate the Mn$^{4+}$/Mn$^{3+}$ ratio and it has been found that the ratio is optimal characteristic of a charge ordered compound.

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Chapter 3
3.1 Introduction

Thermoelectric materials are eco-friendly and are promising candidate for energy conversion and are the focus of research recently. Thermoelectric power or Seebeck coefficient is the rate of change of thermoelectric voltage with temperature. It may be noted here that possible applications of thermoelectric materials are in eco-friendly refrigeration, electric power generation by using waste heat and solar heat, temperature controlled-seats, portable picnic coolers and in satellites [1-4]. For a good thermoelectric material, it must have high thermoelectric figure of merit ZT, for practical applications, \( ZT > 1 \) [4]. Thermoelectric materials can also find applications in the area of refrigeration based on the principle of Peltier cooling [4]. If the efficiency is significantly improved, thermoelectric devices can be a good solution to today’s energy crisis. In order to maximize the thermoelectric figure of merit, a large value of Seebeck coefficient is a pre requisite.

Manganites represent highly correlated electron system and they exhibit a variety of phenomena such as charge, orbital and magnetic ordering, colossal magneto resistance and Jahn-Teller effect [5]. The strong inter-dependence between the magnetic order parameters and the transport coefficients in manganites make much research interest in their thermoelectric power properties [6]. Perovskite class of compounds belonging to the manganites \( \text{RE}^{3+}_{1-x} \text{AE}^{2+}_x \text{MnO}_3 \) [where \( \text{RE} \) is a rare earth metal and \( \text{AE} \) is a divalent cation] series satisfies the requirement of low lattice thermal conductivity. Here, large thermal motion or rattling of rare earth atoms (R) with localized magnetic moments is believed to be responsible for low thermal conductivity of these compounds. The 4f levels in these compounds, lying near to the Fermi energy, create large density of states at
the Fermi level and hence they can exhibit a high Seebeck coefficient [7]. Thus manganites are potential materials for thermoelectric applications [8].

The physical properties of mixed valent manganites are determined by both the amount of substitution and average radius of substituted divalent cations [9]. With substitution, the antiferromagnetic (AFM) interactions arising from Mn$^{3+}$-O-Mn$^{3+}$ tend to compete with the ferromagnetic (FM) interactions resulting from Mn$^{3+}$-O-Mn$^{4+}$ leads to the evolution of various magnetic phases namely AFM, canted AFM (CAFM) and FM making them magnetically diverse. This is illustrated in their rich magnetic phase diagrams [10]. Out of various compositions in the phase diagram, the composition $R_{0.5}A_{0.5}$MnO$_3$ is most interesting [11]. Here, Mn$^{3+}$ and Mn$^{4+}$ are equal in number at this composition and hence ordering of Mn$^{3+}$ and Mn$^{4+}$ species occurs over the lattice, leading to charge ordering and co-existence of antiferromagnetism and ferromagnetism. Below this composition, FM phases are more favourable and above this composition, AFM phases are predominant. As FM and AFM phases co-exist for the charge ordered composition, $x=0.5$, strong competition between these magnetic phases lead to a magnetically frustrated glassy state (spin-glass) which in turn prevents the occurrence of long range magnetic order [12]. Hence the composition corresponding to $x = 0.5$ is critical and physical properties close to this composition are unique. It has been pointed out that various effects such as localization due to charge ordering [13], short range magnetic ordering due to spin-glass [12], electron–electron correlation [14], electron-magnon scattering and electron-phonon scattering strongly modify the temperature dependence of transport properties, especially their thermoelectric power [15-17].

Intermediate bandwidth manganites based on calcium, especially, the charge ordered composition, $La_{0.5}Ca_{0.5}$MnO$_3$, is interesting not only
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from a fundamental angle but also from an applied perspective as they are likely to exhibit colossal thermoelectric power. In this chapter we report the thermoelectric power measurements of La$_{0.5}$Ca$_{0.5}$MnO$_3$ (coded as LCMO5) prepared by high energy ball milling. Emphasis is laid in studying the phenomenon of colossal thermoelectric power observed at low temperature where magnetic ordering present. Phenomena like the co-existences of ferromagnetic and antiferromagnetic phases in La$_{0.5}$Ca$_{0.5}$MnO$_3$ and of charge ordering (CO) is also an interesting aspect in these compounds [18-19]. The valence state of manganese ions and exact composition of powder samples were examined by high resolution core energy level x-ray photoelectron spectroscopy (XPS).

3.2 Experimental

3.2.1 Method of synthesis

Polycrystalline La$_{0.5}$Ca$_{0.5}$MnO$_3$ samples were prepared by high energy ball milling based mechano synthesis technique. Stoichiometric amounts of precursor materials La$_2$O$_3$, CaO and MnO$_2$ were mixed and subjected to milling using a planetary model high energy ball mill (Fritsch pulverisette 7). Milling was carried out for 180 minutes with 400 rotations per minute. The powder obtained after milling was calcined in air at 900°C for 12 hours and then pressed into pellets of cylindrical discs with diameters of 12mm and thickness of 2mm. The pellets were then sintered at 1050°C for 12 hours.

3.2.2 Characterization

The crystal structure of the sample was determined by using a Rigaku D- Max –C, X-ray diffractometer using Cu K$_\alpha$ radiation of 1.54Å and the fine structure was refined by using Rietveld refinement [FullProf Studio, version2]. The magnetic measurements were performed with a Quantum Design- superconducting quantum interference device (SQUID)-
vibrating sample magnetometer (VSM). Low temperature electrical resistivity measurements were carried out using an indigenous resistivity/magnetoresistance setup along with superconducting 8-Tesla magnet. Resistance is measured in longitudinal geometry using a standard four probe technique. The thermoelectric power (TEP) of the sample was estimated by employing a DC differential method over a temperature range of 5K-300K using a home-made set up. To determine the average Mn valence and composition, x-ray photoelectron spectroscopy was performed [Omicron Nanotechnology XPS system with a monochromatic Al K$_\alpha$ radiation (h\nu = 1486.6 eV), source voltage: 15 kV and emission current: 20 mA]. The XPS spectra was then deconvoluted using the Casa XPS program (Casa Software Ltd, UK) in which the background correction was simulated using the Shirley function and peak fitting using a Gaussian-Lorentzian function. The recorded binding energy (BE) spectra were calibrated employing BE of aliphatic carbon at 284.6 eV with a sensitivity of ± 0.2 eV.

3.3 Results and Discussions

3.3.1 Structural studies using XRD

The crystal structure of the sample was determined by using X-ray diffraction. The X-ray powder diffraction pattern of LCMO$_5$ is shown in figure 3.1.a. The XRD peaks correspond to an orthorhombically distorted perovskite structure with Pbmn space group. All peaks are indexed as per ICDD no.46-0513. The average particle size estimated from XRD data using Scherrer’s formula is 34nm. The XRD data have been analyzed by refining the experimental data using a standard Rietveld refinement technique. The Rietveld refined pattern of XRD is shown in figure 3.1.b. The refined lattice parameters determined at room temperature are as follows: a = 5.414 Å, b = 7.683 Å and c = 5.428 Å, which are consistent with earlier reports [20].
occupancy of La$^{3+}$ and Ca$^{2+}$ obtained from the Rietveld analysis is found to be 0.498 and 0.501, respectively.

![XRD pattern for LCMO5.](image)

**Figure 3.1:** (a) XRD pattern for LCMO5. (b) Rietveld refinement performed on LCMO5.

### 3.3.2 Compositional analysis using XPS

Since the mixed valence ratio of manganese (Mn$^{4+}$/Mn$^{3+}$) is a crucial factor in controlling magnetic and transport properties, XPS measurements of charge ordered manganite, La$_{0.5}$Ca$_{0.5}$MnO$_3$, were performed. A typical wide scan XPS spectrum for LCMO5 is shown in figure 3.2. The spectrum exhibits characteristic photoelectron lines of Ca, La, O, Mn and C. The C 1s peak corresponds to the unavoidable contaminant carbon on the top surface of the specimen. For a thorough interpretation of the XPS data, a slow scan of the core energy levels with peaks having highest intensities corresponding to Mn 2p, La 3d, La 4d, Ca 2p and O 1s were recorded. Peaks corresponding to Mn 2p [21], La 3d [22], La 4d [23], Ca 2p [24], and O 1s [25] are consistent with earlier reports. The surface stoichiometry is found to be La$_{0.494}$Ca$_{0.505}$MnO$_3$ where the ratio of La$^{3+}$ and Ca$^{2+}$ ions is 0.978, which is comparable with the value of 0.995 obtained from XRD.
Figure 3.3.a shows the detailed XPS spectrum of Ca 2p which contains a doublet where the line positions of Ca2p$_{3/2}$ and Ca2p$_{1/2}$ are respectively assigned to binding energies 347.5± 0.2eV and 351.2± 0.2eV. The observed spin orbit splitting between Ca2p$_{3/2}$ and Ca2p$_{1/2}$ components is about 3.7eV. The single peak structure of Ca 2p of LCMO reveals that Ca in LCMO exists in a single oxidation state of +2. The binding energies of Ca 2p are almost identical to previous studies [24].

![Figure 3.2: XPS survey scan of LCMO](image)

![Figure 3.3: (a) Ca 2p XPS spectrum  (b) O 1s XPS spectrum](image)

The narrow scan spectrum of the oxygen 1s core level of La$_{0.5}$Ca$_{0.5}$MnO$_3$ is shown in figure 3.3.b. For a perfect Lorentzian- Gaussian curve fitting, oxygen peaks corresponding to O1s can be resolved into two components; one at around 529.9± 0.2eV and the other at about 532.1±
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0.2eV. This doublet peak of O1s agrees with the earlier reports on ABO₃ type perovskites [22, 26-27]. Jaewu Choi et al. observed two peaks at 529eV and 531.4 eV for O 1s in La₀.₆₅Ca₀.₃₅MnO₃ and La₀.₉Ca₀.₁MnO₃ [25]. Daniel Hsu et al. assigned this doublet peak to the chemical shifts in the oxygen core level arising out of two kinds of chemical bonding, the lower binding energy component corresponding to Mn-O bonding and the higher binding energy to La/Ca-O bonding [28]. Since the intensities of peaks 529.9± 0.2 eV and 532.1± 0.2eV are comparable, both these bonds have equal probability of occurrence.

Figure 3.4: XPS spectrum of (a) La3d (b) La4d

Figure 3.4.a shows the resolved spectrum of La 3d doublet. Due to spin–orbit interaction 3d spectrum of Lanthanum consists of two peaks corresponding to 3d₃/₂ and 3d₅/₂ in the range of 830eV-860eV. These doublets show double peak structures in addition to an oxide/hydroxide peak of La compounds by accompanying satellite peaks with comparable intensity to main peaks. The satellite peaks observed have been interpreted in terms of electron transfer process where an outer electron from the lower energy valence p orbital of oxygen ligand is excited to the empty 4f orbital of Lanthanum. Thus each double correspond to states with configurations 3d⁹4f⁰L for lower binding energy main peak and 3d⁹4f¹L for higher binding energy satellite, where L represents oxygen ligand and the underlining
indicates a hole. According to Gauss fitting curves, the lower binding energy peak of La 3d\(_{5/2}\) is found to be at 832.5± 0.2eV and the other at 836.5± 0.2eV corresponds to higher binding energy satellite. Also for La 3d\(_{3/2}\) the lower BE peak state 3d\(^{4}\)f\(^{0}\)L and higher BE satellite state 3d\(^{4}\)f\(^{1}\)L are respectively observed at 849.2± 0.2eV and 853.2± 0.2eV. The spin orbit splitting between 3d\(_{5/2}\) and 3d\(_{3/2}\) is around 16.7eV which is close to the reference values of 16.8eV [22]. The detailed XPS spectrum of La 4d shows that peak of La4d\(_{5/2}\) with satellite peak at 97.4± 0.2eV is observed at 100.5± 0.2eV and the one corresponding to La 4d\(_{3/2}\) is observed at 103.5± 0.2eV, which are also close to the reference values. The XPS spectrum of La 4d is shown in figure 3.4.b.

The mixed valence of manganese in perovskite manganites was determined by analysing the manganese doublet spectra (figure 3.5). The spin–orbit split of manganese 2p peaks correspond to Mn2p\(_{3/2}\) and Mn2p\(_{1/2}\) are located at around 642.1eV and 653.5eV respectively (figure 3.5. a) and the doublet separation is around 11.5eV, which is in good agreement with earlier reported value of 11.8 eV in LCMO [28].

![Figure 3.5: (a) Mn 2p core level XPS spectra including the Mn2p\(_{1/2}\) and Mn2p\(_{3/2}\) core levels and (b) Mn2p\(_{3/2}\) spectrum and fitted curves.](image)

Evidence for the existence of mixed valence states of manganese is obtained from the curve fitting results correspond to the Mn 2p\(_{3/2}\) spectra. It
is evident from figure (3.5.b) that two valence states of manganese are needed for a proper fit. From literature, it is observed that Mn$^{2+}$ peaks are assigned with lower binding energy than Mn$^{3+}$ and Mn$^{4+}$ and also Mn$^{3+}$ peaks are observed at 641.7eV. Hence in the present study, the high binding energy component located at 642.7 ± 0.2eV with FWHM (full width at half maximum) of 2.6eV corresponds to Mn$^{4+}$ while the lower one located at 641.3 ± 0.2eV with FWHM of 2.2eV is related to the presence of Mn$^{3+}$. These values are in close proximity with reference values of 641.3 and 642.8 eV of Mn 2p$_{3/2}$ in La$_{2/3}$Sr$_{1/3}$MnO$_3$ composites [21]. Average concentration of Mn$^{3+}$ obtained by analyzing the Mn 2p doublet structure is found to be 48.28% and that of Mn$^{4+}$ is 51.72%. The mixed valence manganese ratio of Mn$^{4+}$/Mn$^{3+}$ in the present case is ~1.07, which is characteristic of a charge ordered compound.

3.3.3 Magnetic Characterization using FC/ZFC and MH loops

Temperature dependent ZFC and FC magnetization was measured in different applied magnetic fields of 25, 50 and 200 Oe to correlate the co-existence of spin-glass ordering with charge ordering (CO) in LCMO5.

The results are presented in figure 3.6. It can be noted that there is irreversibility in the FC and ZFC magnetisation for temperatures less than 250 K. For higher temperatures, both FC and ZFC magnetisation have similar temperature dependencies. From the FC magnetisation obtained by applying a field of 200 Oe it is clear that a paramagnetic to ferromagnetic transition takes place at around 235 K. Just below this ordering temperature, a slope change in the M-T plot is observed at 200K which is attributed to the charge ordered transition ($T_{CO}$) in this composition [29]. In the FC mode, as the temperature is further reduced, the magnetisation increases resulting in a slope change in M-T curve at around 55K. Thereafter below 50 K, the magnetisation is nearly independent of temperature. On the other hand, the
magnetisation recorded after zero field cooling shows a peak at intermediate temperatures of around 55 K. During zero field cooling from 300 K to 10 K, the moments will be randomly frozen to form a glassy state due to the competing FM-AFM interactions in the system. Subsequent warming of the system in an applied magnetic field will aid the randomly frozen moments to align along the field direction. This result in a rise in ZFC moment and once the thermal energy overrules Zeeman interaction, the ZFC moment starts decreasing resulting in a peak in ZFC magnetisation around the spin-glass transition temperature.

Moreover, from figure 3.6 it can be noted that the irreversible temperature in the FC/ZFC magnetisation increases with decrease in the applied field, which is also a characteristic of a spin-glass system. Dagotta et al. reported an AFM spin ordering referred to as canted AFM spin ordering at low temperatures for charge ordered compositions [12]. Since the nominal
ratio, Mn$^{4+}$/Mn$^{3+}$ ~ 1, LCMO5 qualifies to be a charge ordered composition. The broad peak at low temperatures observed in ZFC can be because of the overlapping of peaks and can be due to both the frustrated glassy transition and the AFM spin ordering [12, 30]. The results indicate that a frustrated magnetic phase has nucleated below T$_{CO}$ due to the co-existence of COAFM and FM phases at very low temperatures [30]. Earlier, Garcia-Landa *et al.* claimed the co-existence of charge order state with a cluster glass state at low temperatures in Gd$_{0.5}$Sr$_{0.5}$MnO$_3$ [31]. Hence at low temperature, in LCMO5, the charge ordered state coexists with a spin-glass state.

The M-H loops of La$_{0.5}$Ca$_{0.5}$MnO$_3$ measured at 10K, 58K and 300K are presented in figure 3.7. Please note that the magnetisation measurements were performed by sweeping the field from +70kOe to -70kOe and vice versa. The magnetisation curves show a non saturating behaviour even after the application of a fairly high magnetic field of 70 kOe. For the M-H curve measured at 10 K, the magnetisation shows two distinct field dependencies. In the high field part, the magnetisation is non saturating and the...
susceptibility is small indicating contributions from a CO antiferromagnetic phase. While in the low field regime, the susceptibility is high similar to that expected from a ferromagnetic phase. Further, a hysteresis can be observed in the high field part of the M-H curve (inset (a) in fig 3.7). This indicates the existence of a meta magnetic FM phase formed by the partial transformation of the COAFM phase under high field. This meta magnetic transition is associated with the quenching of the CO state and emergence of FM ordering. The appearance of a meta magnetic transition for LCMO5 is a clear signature of the coexistence of FM and COAFM phases and the competing FM-AFM interaction in LCMO5 results in a spin-glass transition at T<50K. Earlier reports on calcium doped praseodymium manganites with x= 0.3, 0.4, 0.5 strongly supports the presence of such meta magnetic transitions at higher fields [18, 32]. Previous reports on the meta magnetic transition in manganites is based on the coexistence of a FM phase in the COAFM matrix [32-34]. When the temperature is increased to 58K, signatures of this meta magnetic transition is still visible although the high field hysteresis is reduced due to thermal excitation. At 300 K, the measured M-H curve for LCMO5 is characteristic of a typical paramagnet. The hysteresis loop of LCMO5 at 10K exhibits a coercive field of 260 Oe, whereas at 58K the coercivity decreases to 150 Oe (inset b in fig 3.7). This coercivity decrement with increasing temperature also supports spin-glass like transition in LCMO5. It is to be noted that preparative conditions do alter size/ grains of particles of magnetic materials and therefore, preparative conditions do have an indirect bearing on the coercivity of these samples [35-36]. Earlier, Iniama et al reported on the particle size dependence of LCMO5 on coercivity [37]. They reported that coercive field is negligible for bulk samples, whereas with decreasing particle size, coercivity enhances.
3.3.4 Thermoelectric power studies

The temperature dependent thermoelectric power (S) of La$_{0.5}$Ca$_{0.5}$MnO$_3$ measured in the temperature range from 5K to 300K is shown in figure 3.8. The temperature dependence of S is more pronounced below the Curie temperature, and a further decrease in temperature results in a broad peak at around 58K exhibiting a colossal thermoelectric power of -80mV/K. It may be noted that a large value of the order of 80mV/K for TEP is not found to be reported in literature. Negative thermoelectric power throughout the whole temperature region indicates the presence of electrons as charge carriers which is consistent with earlier reports on thermoelectric power of heavily doped calcium lanthanum manganites [38-39]. The most important temperature region for this composition is T<T$_C$ especially T<200K (T$_{CO}$) where the system enters into the charge ordered state. The variation of electrical resistivity with temperature as shown in the inset of figure 3.8 indicates that there is a semiconductor like behaviour with an upturn at charge ordered (CO) state temperature. In addition to this, a weak dependence of resistivity with temperature below 120K indicates the existence of Kondo behaviour.

![Figure 3.8: Temperature dependence of thermoelectric power from 5K to 300 K. The inset shows the resistivity as a function of temperature.](image)
3.3.4.1 Low temperature behaviour

A major variation in thermoelectric power is observed in this charge ordered region, where for temperatures $T<120K$, this variation of thermoelectric power is maximal and exhibit a peak value of $-80mV/K$ at $58K$. For this specific region, the charge ordered state co-exists with the spin-glass state as deduced from ZFC magnetization measurements. Hence the above mentioned prominent variation in thermoelectric power with respect to temperature below $T_C$ has been analyzed based on the charge ordered spin-glass state.

There is no general relationship to interpret TEP corresponding to the FM region. Earlier Blatt et al. explained the broad peak observed in $S$ at low temperature for iron by magnon drag [40]. Later Mandal interpreted the low temperature TEP data of divalent doped manganites by adopting a spin wave theory giving due attention for magnon drag interactions [6]. He analyzed the TEP data in the FM phase using an expression

$$S = S_0 + S_{3/2} T^{3/2} + S_4 T^4$$  \hspace{1cm} (3.1)

where $S_0$ ($S$ at $T=0$) is a constant which accounts for truncating the low temperature thermoelectric power data, $S_{3/2} T^{3/2}$ is attributed to the magnon drag contribution which strongly influences the low temperature TEP data in manganites and $S_4 T^4$ is accredited to the spin wave contribution. The present TEP data in the low temperature region, especially where CO co-exist with a spin-glass, the prominent peak observed at $58K$ cannot be completely fitted by the model presented by Mandal. Since LCMO5 is a critical composition which lies in the boundary between the FM and COAFM phase of this series, FM and COAFM phases co-exist leading to a magnetically frustrated glassy state.

In the present investigation, the temperature corresponding to the colossal thermoelectric power peak value of $\sim 80mV/K$ observed is close to
the spin-glass transition temperature. FC/ZFC magnetization measurements in the charge ordered spin-glass region (T<120K) indicates the existence of both frustrated glassy state and a AFM spin ordering. Thus by both glassy and AFM spin ordering, charge carriers are localized at the sites. Hence the role of competing AFM phases due to charge ordering, and spin-glass becomes more prominent in this region. Below this transition temperature, TEP tends to decrease which can be due to an increase in magnetic ordering with decrease in temperature. Earlier reports on thermoelectric power of spin-glasses showed giant values at low temperatures [41-43]. Later K.H Fischer modelled the TEP in the spin-glass region by considering a Kondo term, $S_2 T^2$, and a resonance term, $S_1 T$, with opposite sign which lead to a change of sign of TEP at a characteristic temperature $T_0$ [44]. But in the present system, there is no change of sign of TEP. So the term corresponding to this sign change, the resonance term, is not considered. Therefore, it is possible to explain the observed prominent peak at 58K by incorporating Kondo properties of the spin-glass along with magnon scattering as proposed by Mandal. Thus in the low temperature region (T<120K) we have analyzed the TEP data by using the expression

$$S = S_0 + S_{3/2} T_{3/2}^3 + S_2 T^2 + S_4 T^4$$

(3.2)

Figure 3.9: Variation of $S$ with $T$ (a) at T<120K, (b) at 120K<T<T_c. The solid line gives the best fit to equations.
The experimental data fits well as per equation 3.2 and is shown in figure 3.9.a and the fitted parameters are listed in table 3.1. It can be seen that the TEP in the very low temperature regime not only consists of term corresponds to magnonic origin but also have a charge ordered spin-glass contribution as well. However, to explain TEP data in the region $120K<T<T_C$ instead of the spin-glass contribution, a phonon drag term is included in Mandal’s model. Fitting of TEP in the remaining CO regime using the following equation

$$ S = S_0 + S_{3/2} T^{3/2} + S_3 T^3 + S_4 T^4 $$  \hspace{1cm} (3.3)

points out that in addition to magnon drag produced by electron-magnon interaction, a $T^3$-dependence of $S$ due to phonon drag produced by electron-phonon interaction is also significant in this region. The TEP data measured in the temperature range $120K<T<T_C$ fitted to equation 3.3 is shown in figure 3.9.b. From the fitted values the magnon drag contribution is more prominent since due to charge ordering the magnetic phase is transformed to AFM. Thus the combined contribution of both spin-glass and charge ordering gives rise to a colossal thermoelectric power in the low temperature regime ($T<T_C$).

Table 3.1. The best fit parameters of the experimental TEP data measured in the temperature range $T<120K$ and $120K<T<T_C$. NC stands for no contribution.

<table>
<thead>
<tr>
<th>Temperature region</th>
<th>$S_0$</th>
<th>$S_{3/2}$</th>
<th>$S_2$</th>
<th>$S_3$</th>
<th>$S_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T&lt;120K$</td>
<td>-61.12</td>
<td>1.27</td>
<td>-0.018</td>
<td>NC</td>
<td>7.49E-7</td>
</tr>
<tr>
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<td>0.69</td>
<td>NC</td>
<td>-2.15E-5</td>
<td>5.98E-8</td>
</tr>
</tbody>
</table>

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3.3.4.2 High temperature behaviour

The charge ordered composition LCMO5 exhibits an appreciable Seebeck coefficient in the high temperature region (T>T_c). Due to the optimal Mn^{4+} - Mn^{3+} concentration in LCMO5, distortion became prominent so that the charge carriers are trapped and gives rise to polarons. Hence the transport mechanism involves hopping through polarons. The thermoelectric power data in the high temperature region (T>T_c) is interpreted by using Mott’s well known equation [45] based on polaron hopping.

\[
S = \frac{k_B}{e} \left[ E_s + \alpha \right]
\]

where \(k_B\) is the Boltzmann constant, \(e\) is the electronic charge, \(E_s\) is the activation energy for conduction obtained from thermoelectric power data and \(\alpha\) is a constant of proportionality between the heat transfer and kinetic energy of an electron. \(\alpha < 1\) implies the existence of small polarons, while for \(\alpha > 2\) suggests that the conduction involves large polarons [46]. From the slope of the straight line fit to the S versus 1/T plot, activation energy of \(E_s = 17.14\,meV\) and from the y intercept, the constant \(\alpha = 0.315\) is obtained. The value of \(\alpha < 1\) indicates the presence of small polaron carriers in the high temperature region. Figure 3.10 shows the best fit curve of S versus 1/T plot.
Figure 3.10: Variation of S with 1/T for T > T_C. The solid line gives the best fit to equation (3.4).

3.4 Conclusions

The single phase charge ordered composition La_{0.5}Ca_{0.5}MnO_3 was synthesized by high energy ball milling. The sample possessed a distorted orthorhombic perovskite structure with a Pbmn space group. A colossal thermoelectric power of -80mV/K at 58K was observed. Both the surface composition and the optimal Mn^{4+}-Mn^{3+} concentration in charge ordered LCMO5 was examined by XPS analysis. A strong competition between the FM and AFM order due to charge ordering results in a spin-glass state in the temperature regime T<120K. The observed colossal thermoelectric power was explained based on the charge ordered spin-glass state. The colossal Seebeck coefficient value at 58K was explained by incorporating Kondo properties of the spin-glass along with magnon scattering as proposed by Mandal. The Kondo dependence is clearly visible from the resistivity variation. TEP data in the charge ordered region (120<T<T_C) is explained by including a phonon drag term in Mandal’s model, instead of a spin-glass contribution. Thermoelectric power in the region above the Curie temperature is due to the presence of small polaron carriers in the high temperature
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region. The frustrated glassy state and AFM spin ordering at low temperatures leads to localization of charge carriers which manifests in the form of colossal thermoelectric power.

References

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Chapter 4

Size effect on the colossal thermoelectric power in charge ordered small bandwidth manganites based on Gd-Sr

Earlier we observed colossal thermoelectric power in charge ordered intermediate bandwidth manganite La$_{0.5}$Ca$_{0.5}$MnO$_3$ and was explained based on charge ordering and occurrence of spin glass states. With a view to extending such a study on small bandwidth Gd-Sr manganites, both unmilled and milled forms of Gd$_{1-x}$Sr$_x$MnO$_3$ (x =0.3, 0.5, and 0.6) samples were prepared. This chapter discusses the size effect on the contribution to thermoelectric properties from different scattering mechanisms. Charge ordered compositions, both milled and unmilled forms, exhibited colossal thermoelectric power. Compared to unmilled samples, thermoelectric power of charge ordered milled samples exhibit higher values. Emphasis is laid in studying the role of grain boundary and grain size on different scattering mechanisms responsible for colossal thermoelectric power in charge ordered manganites. The absolute value of thermoelectric power almost doubled in the case of milled samples and attained a maximum value of -69 mV/K at 42K, where a spin glass transition takes place. In order to explain the occurrence of transition at ~42K, Field cooling and Zero field cooling magnetic measurements were conducted.

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