CHAPTER 2

Experimental Techniques
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2.1. Introduction

In this chapter we present experimental techniques used for synthesis, characterization and transport properties of manganite samples used in the present work. All these polycrystalline manganites are synthesized using conventional solid state reaction method which is described in this chapter and structural characterization is carried out by using X-ray diffraction (XRD). To obtain the metal-insulator transition temperature ($T_{MI}$) and to study the effect of magnetic field on resistivity, the electrical resistivity and magneto-resistance measurements were carried out using a superconducting magnetic system (Oxford Spectromag)- at magnetic fields over a temperature range 2.5-350K using four probe method. The details of these measurements are given in this chapter. DC magnetization measurements were carried out using MPMS SQUID VSM dc Magnetometer (Quantum Design) and are described here. Thermal conductivity and thermo-power measurements were done using direct pulse technique. Specific heat measurements were carried out using ac calorimeter. The details of thermal property measurements are provided in this chapter.

2.2. Sample preparation:

There are several methods for preparation of manganites. They are divided into two types viz. (i) Solid state reaction method (dry process) and (ii) Co-precipitation method (wet process). In the solid state reaction method, the oxides or carbonates of the constituents are taken in the form of powder. The stoichiometric ratio of various compounds is weighed and the mixture is well ground. Intermediate grinding confirms both uniform mixing and fineness of grain size. The well ground powder is heated at temperature of about 1000°C to decompose carbonates into oxides. This heat treatment is called calcination. After several intermediate grindings the powder is pressed in the form of pellet which is sintered in temperature range 1000-1300°C. The mixing is also very important which helps in minimizing the diffusion distance at low temperatures. The material decompose into fine powders after first firing. The calcination helps in removal of volatile components which minimizes the internal stress which can lead to cracks. Solid state reaction involves ionic diffusion process and it is a slow process it requires high thermal energy. But in the co-precipitation method, the constituent compounds
are nitrates. These are precipitated in their carbonate form, followed by heating the precipitate to remove water. In the present studies, all samples are prepared by using standard ceramics solid state reaction method because of its simplicity. The pristine compounds used in preparation were mainly elements in oxide or carbonate form taken in stoichiometric amounts with minimum of 99.99% purity. High purity stoichiometric amounts of materials were taken in appropriate proportions and mixed thoroughly with an agate mortar and pestle. This was followed by calcinations at different temperatures with intermediate grindings to ensure the homogeneity of the material. Then the pellets were sintered at temperature between 1000°C to 1400°C for longer duration to overcome the slow kinetics of ion diffusion across particle boundaries. In order to ensure compound homogeneity the products were slowly cooled from high temperature by keeping the samples in closed furnace.

2.3. Sample Characterization Techniques

Structural characterization:

There are three main categories of physical techniques which may be used to characterize the crystals: these are diffraction, microscopic and spectroscopic techniques. Diffraction is a very powerful technique to characterize and determine the structure of crystalline materials. Three types of radiation are used for crystal diffraction studies viz. X-rays, electron and neutrons. In the present work, we have used X-ray diffraction to determine the crystal structure of various samples of manganites.

2.3.1. X-ray Diffraction (XRD):

It is well known that crystals are built up of a regular arrangement of atoms in three dimensions, and they can represented by a repetition of a smallest unit called unit cell which shows the full symmetry of the crystal structure. Since in X-ray diffraction, the wavelength of X-rays is comparable to the inter-atomic spacing (d) in the crystal, atoms scatter and reflect the incident X-rays so a diffraction pattern can be generated. The crystal structure can determined by recording the analyzing the diffraction pattern produced by X-rays. For diffraction experiments, monochromatic beam of X-rays is desired and the X-ray wavelength commonly employed is the characteristic $K_{\alpha}$ radiation, $\lambda=1.5418\text{Å}$ emitted by copper. $K_{\alpha}$ is most intense and filter out all the other wavelengths. There are two approaches
to treat diffraction by crystals, they are:

The Laue equations

This method provide a rigorous and mathematically correct way to describe diffraction by crystals. However this method is cumbersome to use.

Bragg’s law

Figure 2.1 shows schematic picture of X-ray diffraction by lattice. The figure shows two rays incident at an angle \( \theta \) (called glancing angle) and the reflected rays are also shown in the figure. The path difference between the rays from successive planes is given by \( 2d \sin \theta \) If the reflected rays interfere constructively which satisfy the Bragg reflection condition \( 2d \sin \theta = n \lambda \), where \( d \) is the spacing between the parallel planes, \( 2 \theta \) is the angle between collimated incident X-ray beam and the diffracted beam, \( n \) is the order of diffraction and \( \lambda \) is the wavelength of the incident beam. Using Bragg’s law, the symmetry and lattice parameters of a unit cell of a material can be obtained by analyzing the position of Bragg’s peaks and peak intensity. To relate the unit parameters and atomic planes in a crystalline structure the concept of Miller indices can be used. The Miller indices of a plane are commonly written as \((hkl)\), where \( h = a / x \), \( k = b / y \) and \( l = c / z \) where \( a \), \( b \), and \( c \) are lattice parameters of the unit cell and \( x \), \( y \), and \( z \) are the points where the plane intersects the crystallographic axes.

Fig. 2.1. Diffraction of beam from a set of lattice planes
A crystalline powder sample consists of a large number of randomly orientated crystallites. These crystals will take up every possible angular position with respect to the incident beam and therefore the diffracted beams will be emitted as cones of radiation. Thus an X-ray powder diffraction pattern is a set of peaks or lines, each of different intensity. For a given substance the line positions are fixed and characteristic of any sample. Each crystalline substance has its own characteristic powder diffraction pattern which is used for its identification. The standard patterns are given in Powder Diffraction File (known as JCPDS file). The powder X-ray method is used to check impurities present in the specimen. Using a least squares minimization procedure, unit cell parameters accurate to four or five significant figures can be obtained. Crystal structures are solved by analyzing the intensities of diffracted X-ray beams. X-ray powder diffraction may be used to measure average crystal size in a powdered sample, provided the average diameter is less than about 2000Å. The lines in a powder diffraction pattern are of finite width if the particles are very small. The broadening in lines increases with decreasing particle size.

**Basic features of XRD experiment:**

A schematic of the experimental set up is shown figure. 2.2.
In X-ray diffractometer, the mechanical assembly that makes up the sample holder, detector arm and associated gearing is referred to as goniometer. The distance from the X-ray focal spot to the sample is the same as from the sample to the detector. If we drive the sample holder and the detector in a 1:2 relationship, the reflected (diffracted) beam will stay focused on the circle of constant radius. The detector moves on this circle. For the THETA : 2 THETA Goniometer, the X-ray tube is stationary, the sample moves by the angle $\theta$ and the detector simultaneously moves by the angle $2\theta$. At high values of $\theta$ small or loosely packed samples may have a tendency to fall off the sample holder. In powder or polycrystalline diffraction, a sample should have smooth plane surface. In the present investigation, Bruker D8 Advance X-ray diffractometer is used as shown in figure 2.3.

![Bruker D8 Advance X-ray diffractometer](image)

**Fig.2.3. Bruker D8 Advance X-ray diffractometer**

The sample in the form of powder, is fixed on the sample mounter. The sample mounter is kept at the center of the diffractometer. The X-rays are produced using a sealed tube and the wavelength of X-ray is about 1.542Å (Cu K-alpha). Standard sample holder of the diffractometer is a 9 sample changer, making it possible to measure up to 9 samples in a series. The X-rays were detected using a fast counting detector based on Silicon strip...
technology (Bruker Lynx Eye detector) in the $2\theta$ range of 20°-80° with step size of about 0.02. The photograph of BRUKER AXS D8 ADVANCE system is depicted in figure 2.4. The sample preparation for X-Ray Powder Diffraction (XRPD) is the universal approach for specimen preparation is as follows: thinly coating a plate (e.g. normal quartz) with some kind of gelatin and flattening it, sieving the finely ground powder onto the plate and gently tapping of shaking the plate to make the powder spread out on it uniformly, inverting the plate to dislodge the excess powder, repeating steps and until enough powder adheres to the gelatin and waiting for the gelating to dry.

![Photograph of BRUKER AXS D8 ADVANCE system](image)

**Fig. 2.4. Photograph of BRUKER AXS D8 ADVANCE system**

### 2.3.1.1. Rietveld Refinement

Rietveld refinement is a technique which was devised by Hugo Rietveld [178] which is used in the characterization of any crystalline material. The neutron and x-ray diffraction of powder samples results in a pattern which are characterized by reflections (peaks in intensity) at certain positions. The height, width and position of these reflections can be used to
determine many aspects of the structure of any material. The Rietveld method uses a least squares approach to refine a theoretical line profile until it matches the measured profile. To refine crystal and magnetic structures from X-ray diffraction pattern it is customary to use Rietveld refinement method [178]. *WINPLOT* is a graphic program for analysis of powder diffraction pattern. Graphical display on a computer screen of raw powder diffraction patterns is great interest as it provides to have a rapid and realistic idea of quality of synthesized sample in terms of sample crystallinity and impurity peaks. Visualization of agreement between experimental and those calculated from a physical model implemented in particular software (for example a Rietveld type program) is a primary necessity to estimate the crystal structure of any sample. It can be used to plot raw and normalized data files coming from Rietveld files created by the Rietveld type refinement program (*fullprof*): edition of pcr input file, plot Rietveld type plots. In particular it can be considered as a software partner of the refinement program *Fullprof* [179].

*Fullprof* program has been developed for the Rietveld analysis of X-ray powder diffraction data. For starting a profile refinement, the best way is to copy one of the PCR files accompanying the distribution of *FullProf*, and modify it according to the user’s case: x-ray diffraction data. The provided PCR files can then be used as templates. An important aspect is the format of the data file that must be correctly given before attempting any kind of refinement. The control of the refined parameters is achieved by using codewords. The order of refining the parameters was: the scale factor, the zero point for $2\theta$, five of the background parameters, the cell parameters, three of the peak shape parameters, the $z$ co-ordinates, the isotropic displacement parameters, the occupation numbers, the fourth peak shape parameter, the anisotropic displacement parameters and the last background parameter. A few different routes to convergence were tried to confirm an optimal result. The $R$ factors are good indicators if a route is not converging to a reliable result. Overlaps are seen between Bragg reflections for lower-symmetry materials due to the polycrystalline nature of a powder sample in most of powder diffraction patterns. Instead of analyzing each individual reflection or resolving the reflection overlaps, the Rietveld method is performed using a curve-fitting procedure by considering the observed intensity $y_i(\text{obs})$ of each equally spaced steps $i$ over the entire pattern including the background intensity and the sum of the contribution of reflections close to the $i$ powder pattern step:

$$y_i(\text{obs}) = y_i(\text{background}) + \sum y_i(\text{Bragg}) \quad (2.1)$$
Chapter 2  

Electrical, magnetic and thermal properties of Bi doped \( \text{RE}_{0.6-x}\text{Sr}_{0.4}\text{MnO}_3 \) and \( \text{RE}_{0.7-x}\text{Sr}_{0.3}\text{MnO}_3 \) (\( \text{RE}=\text{Pr, La} \)) manganites

The fitting results can be estimated by examining a plot of the difference between observed and calculated patterns. There are several numerical terms that can be used to estimate the goodness of the least-square refinements.

\[
R\text{-pattern} \quad \text{R}_P = \frac{Y_{i(\text{obs})} - Y_{i(\text{calc})}}{Y_{i(\text{obs})}} \quad (2.2)
\]

\[
R\text{-weight pattern} \quad \text{R}_{wp} = \frac{\sum w_i Y_{i(\text{obs})} - Y_{i(\text{calc})}^2}{\sum w_i Y_{i(\text{obs})}^2}^{1/2} \quad (2.3)
\]

\( Y_{i(\text{obs})} \) is observed intensity at angular step i and \( Y_{i(\text{calc})} \) is corresponding calculated intensity and \( w_i \) is weight function

\[
\text{Bragg factor} \quad \text{R}_{\text{Bragg}} = \frac{\sum |I_{jo} - I_{jc}|}{\sum |I_{jc}|} \quad (2.4)
\]

\( I_{jo} \) and \( I_{jc} \) are observed and calculated integrated intensities for the different Bragg peaks j.

\[
\chi^2 = \frac{\text{R}_P}{\text{R}_{wp}}^2 \quad (2.5)
\]

A good fit with the refined structure model will accompany with low residual value. A typical result of refinement using FullProf program is given in Appendix A.

2.3.2. Resistivity/Magnetoresistance set up:

Conventional four probe method is used to measure resistivity of the samples under present investigation. The same technique was also used to measure magneto-resistance of samples. A constant current was passed through the sample, as shown in figure 2.5.

![Fig. 2.5. Schematic diagram of four probe configuration](image_url)
Chapter 2

Electrical, magnetic and thermal properties of Bi doped RE_{0.6-x}Sr_{0.4}MnO_3 and RE_{0.7-x}Sr_{0.3}MnO_3 (RE=Pr, La) manganites

The Ohm’s law (R=V/I) was used to find the dc resistance of the sample. The dc resistivity was calculated using the expression, \( \rho = RA/L \) where \( A \) applied to the sample across two ends and the voltage was measured across the middle contacts is the area of the sample and \( L \) is the distance between the voltage probes.

An insert used for resistivity and MR measurement is shown in figure 2.6. The general purpose variable temperature insert consists of a sample holder of square OHFC copper block. On the top of each face of copper block an aluminum foil is fixed with GE varnish to insulate electrically the samples from the sample holder. Four samples can be loaded on each face. At the four corner of the block, copper strips are attached, on which PCB strips has been fixed for electrical terminals.

![Fig.2.6. Schematic diagram of Resistivity/Magnetoresistance Insert [180]](image)

On the SS tube ten equally spaced copper baffles of thickness 1mm and diameter 36mm were brazed. These baffles act as a radiation shield and utilize the enthalpy of outgoing Helium gas for efficient cooling. The copper wires of SWG 44 (0.081 mm diameter) are used
as electrical leads from the sample and temperature sensor to the room temperature end of the insert. The voltage and current leads are pair-wise twisted separately, for each sample holder.

**Fig. 2.7. Schematic diagram of General Purpose Variable Temperature Insert [180]**

In this insert, 16 samples can be loaded at a time. It can be used for resistivity measurements in absence of magnetic field in the temperature range 1.5-300K, with the general purpose variable temperature insert (VTI). The schematic diagram of General Purpose Variable Temperature insert is shown in figure 2.7. It is made up of two co-axial thin wall tubes of outer diameters 37mm and 51mm. To prevent collapsing of outer tube under vacuum, six SS rings are used for reinforcement from inside the tube. To thermally isolate the sample space from the liquid helium bath, the spacing between two tubes is evacuated. The sample space is connected to liquid helium bath through a fine copper-nickel capillary tube of specific length to have efficient cooling. The space between the two tubes is connected with a diffusion pump through long bellow fitted with a valve and the sample space is connected to oil free rotary pump through a two meter long above. To start, space between the two tubes...
is evacuated to a vacuum of the order of \(10^{-6}\) torr. The insert is slowly moved inside the liquid helium storage Dewar, till it reaches the liquid helium level. At the same time sample space is continuously pumped. The liquid helium moves through the capillary to the sample space and reduces the sample space temperature. The temperature of the sample space is controlled by cryogenic temperature controller using a heater and a temperature sensor mounted at the base of sample space. When the measurements above 100K are required the insert is lifted up to reduce the helium losses due to boiling. Figure 2.8 shows schematic diagram of electrical connections between the various electronic instruments. Lakeshore temperature controller (DRC-93CA) is used for measuring and controlling the temperature of the sample holder. Keithley Switching System is used for selecting the different samples. A nonovolt scanner and card (model 7168) is used for switching between the voltage leads of different samples and a general-purpose scanner card for switching between the current leads. Keithley source meter (model 7056) is used to pass current through current leads and voltage across the voltage leads is measured by Keithley sensitive digital voltmeter. The measurements start by controlling temperature and the scanner selects a particular sample. Then through the current lead, a specified current is passed through the sample and voltage is measured across voltage leads. This process continues for other samples also. Once the measurement of all the samples is completed the temperature controller sets next temperature. The process of measurement is repeated after achieving the required temperature stability. The collected data is plotted online as resistance versus temperature on a computer monitor.

\[
\rho = \frac{A}{L}R \tag{2.6}
\]

The magneto-resistance is defined as,

\[
MR(\%) = \left(\frac{\rho_0 - \rho_H}{\rho_H}\right) \times 100 \tag{2.7}
\]

It can be measured in two different modes: (i) Magneto-resistance as a function of temperature at constant magnetic field which is obtained from the measured resistance as a function of temperature in zero field and in presence of constant magnetic field. (ii) Magneto-resistance as function of magnetic field at constant temperature can be obtained by measuring the resistance at various magnetic fields at that temperature.
Fig. 2.8. Block diagram of Resistivity/Magnetoresistance set up [180]
Photograph of magneto-resistance set up is shown in figure 2.9.

![Photograph of magneto-resistance set up](image)

**Fig.2.9. Photograph of magneto-resistance set up**

### 2.3.3. Magnetic Measurements:

Study of magnetization with temperature in zero field and field cooling at temperature 2-350K (100 Oe) and variation of magnetization with magnetic field 0-80 kOe at 5K and 200K were performed using a Quantum Design Magnetic Property Measurement System (MPMS), which contains a Superconducting Quantum Interference Device (SQUID). The SQUID detection system consists of a superconducting ring with a weak link which is capable of amplifying any small changes in magnetic field into large electrical signals. The ring is coupled with a superconducting sensing coil, which surrounds the sample, by superconducting circuitry. The sample moves through the detection coils in discrete steps and the high uniform magnetic field in the magnetometer is generated by a superconducting magnet. The working principle of VSM is based on Faraday’s law of induction, which states that an *e.m.f.* is induced in a conductor by a time-varying magnetic flux. This electric field can be measured and provides us information about the changing magnetic field. Using VSM the hysteresis loop parameters namely saturation magnetization ($M_s$), coercive field ($H_c$), remanence ($M_r$).
Fig.2.10. Schematic diagram of Vibrating Sample Magnetometer

The schematic diagram of vibrating sample magnetometer is given in figure 2.10. In a VSM, the sample to be studied is placed in a constant magnetic field. If the sample is magnetic, this constant magnetic field will magnetize the sample by aligning the magnetic domains or the individual magnetic spins, with the field. The stronger the constant field, the larger will be the magnetization. The magnetic dipole moment of the sample will create a magnetic field around the sample, usually called the stray field. As the sample is moved up and down, this magnetic stray field changes as a function of time and can be sensed by a set of pick up coils. A transducer converts a sinusoidal ac drive signal provided by a circuit located in the console into a sinusoidal vertical vibration of the sample rod and the sample is thus made to undergo a sinusoidal motion in a uniform magnetic field. Coils mounted on the pole pieces of the magnet pick up the signal resulting from the sample motion. The alternating magnetic field will cause an electric field in the pickup coil as per Faraday’s law of induction, the current will be proportional to the magnetization of the sample. The greater the magnetization, the...
greater is the induced current. The induction current is amplified by a trans-impedance amplifier and a lock-in amplifier. The various components are interfaced via a computer. The system can tell how much the sample is magnetized and how magnetization depends on the strength of the constant magnetic field can be done by controlling and monitoring software. For particular field strength, the corresponding signal received from the probe is translated into a value of magnetic moment of the sample. When the constant field varies over a given range, a plot of magnetization versus magnetic field strength is generated. The temperature control insert of the MPMS SQUID VSM is a vacuum-insulated chamber into which cold helium is drawn, through a variable flow valve, for purposes of cooling the sample chamber with pumped helium to temperatures as low as 1.8 K. A finely tuned flow impedance and temperature control software allows continuous operation at 1.8 K as well as smooth temperature control through the 4.2 K liquid helium boiling point. Heaters on the sample chamber can raise the temperature as high as 400 K. A thermal shield, anchored to a liquid nitrogen tank, intercepts heat from a warm sample chamber and minimizes liquid helium consumption when operating at higher temperatures. The MPMS SQUID photograph is shown in figure 2.11. VSM utilizes a 7 Tesla, superconducting, helium-cooled magnet and a hybrid digital/analog magnet controller designed specifically for the SQUID VSM to achieve precise and quiet control of the magnetic field. SQUID precision in a magnetic measurement requires a stable magnetic field. The SQUID VSM accomplishes rapid switching between charging and discharging states and stable fields with a unique superconducting switching element called the Quick Switch. The high open state resistance and low thermal mass of the Quick Switch design also helps to minimize liquid helium consumption when ramping magnetic field. The nitrogen shield in this design absorbs a large amount of room temperature heat that would otherwise be conducted to the helium bath. Zero Field Cooled (ZFC) measurements provide a means of investigating various magnetic interactions. First the sample is cooled to liquid helium temperatures under zero applied magnetic fields. Then small uniform external field is applied and the net magnetization is measured while heating the sample at a constant rate. For small magnetic field, they will tend to magnetize along the preferred crystal directions in the lattice, thus minimizing the magneto-crystalline energy. Since the orientation of each crystallite varies randomly the net moment of the system will be zero. Even when a small external magnetic field is applied the moments will remain locked into the preferred crystal directions, as seen in the low temperature portion of the ZFC curve.
Chapter 2

Electrical, magnetic and thermal properties of Bi doped RE_{0.6-x}Sr_{0.4}MnO_3 and RE_{0.7-x}Sr_{0.3}MnO_3 (RE=Pr, La) manganites

As the temperature increases more thermal energy is available to disturb the system. Therefore more moments will align with the external field direction in order to minimize the Zeeman energy term. In other words, thermal vibration provides the activation energy required for the Zeeman interaction. Eventually the net moment of the system reaches a maximum when the greatest population of moments has aligned with the external field. The peak temperature is called blocking temperature \( T_B \) which depends on particle volume. As temperature reaches above \( T_B \), thermal vibrations become strong enough to overcome the Zeeman interaction and thus randomize the moments. Field cooled measurements proceed in a similar manner to ZFC except (TEP) that the constant external field is applied while cooling and heating. The net moment usually measured while heating the sample. However, the Field Cooled (FC) curve will diverge from the ZFC curve at a point near the blocking temperature. This divergence occurs because the spins from each particle will tend to align with the easy crystalline axis that is closest to the applied field direction and remain frozen in that direction at low temperature.

Fig.2.11. Photograph of an actual MPMS SQUID VSM at Quantum Design
2.3.4. Thermal Measurements:

2.3.4.1. Thermo-electric Power:

In the present investigations, we have measured thermoelectric power using a differential DC method with oxygen free highly conducting (OFHC) copper [181-182] as reference in the temperature range 10-350K. In the present set up the samples may be of small size ceramic, metallic, or semiconductor material in the form of single crystal, ribbon, wire or small bar. Typically, a pellet of about 5 mm diameter having 0.5–2mm thickness is ideal as is usually preferred for scientific investigations. The sample with freshly cleaned surfaces was secured between two cylindrical OFHC blocks using an SS spring and an axial brass screw as shown in figure 2.12.

Fig.2.12 (a). Schematic diagram of the general-purpose vacuum insert. (b). Photograph of the bottom portion of sample holder and the radiation shield for TEP measurements. (c). Schematic diagram of thermoelectric power measurement setup connected to computer-interfaced system.

The two junctions of the chromel-Au–Fe (0.07%) thermocouple were anchored thermally to the two OFHC blocks to which electrical leads were attached that enable good electrical
contacts for the thermally generated potential difference ($\Delta V$) measurements. A temperature controller was used to maintain the temperature difference ($\Delta T$) between the two OFHC blocks using the chromel-Au–Fe (0.07%) thermocouple and a heater wire wound on the lower OFHC block [Fig. 2.12(c)]. One can set $\Delta T$ can be set to a desired value. A silicon diode and another heater anchored to the upper OFHC block were connected to another temperature controller to sustain a desired controlled sample temperature (10 mK). The nanovoltmeter coupled through a nano volt scanner card measures the $\Delta V$ and the $\Delta T$ via the chromel- Au–Fe(0.07%) thermocouple. The sample holder was attached to a heat sink via three SS rods and a hylum disk [Fig.2.12(b)]. A removable cylindrical OFHC jacket fits at the bottom of the brass flange as a radiation shield. The sample holder with wiring assembly is loaded in the cryostat. The $TEP$ data $S_{\text{meas}}=\Delta V/\Delta T$ were recorded through a personal computer for a desired temperature step and range [183]. The Seebeck coefficient of the copper reference $S_{Cu}$ is subtracted from the measured $S_{\text{meas}}$ such that the sample $S$ is given by $S=S_{\text{meas}}-S_{Cu}$. The reliability of the $S_{Cu}$ data used for subtraction from the measured $S_{\text{meas}}$ has been satisfactorily proven as the measured data on the standard samples match the published data.

Fig.2.13. Photograph of thermopower set up
The fabricated general purpose vacuum insert (cryostat) that can be fitted inside a commercially available 60 l liquid helium or nitrogen Dewar. The cryostat is essentially fabricated using an SS tube (93 cm Lx5 cm ID x 0.05 cm T) brazed with (10 cm Lx5.1 cm IDx0.2 cm T) OFHC solid rod made as cup at the bottom, a ball valve, and a vacuum port near the neck with the top-end fitted with an appropriate sample holder [Fig.2.12(a)]. The cryostat with a vacuum maintained inside better than $10^{-6}$ mbar houses the sample holder assembly, either resistivity or thermo-power, up to its neck. The advantage for the ball valve and a vacuum port near the neck assembly is that they allow us to load and unload the sample or its holder with ease, fast, without disturbing the vacuum inside the cryostat. The photograph of the thermo-power set up is shown in figure 2.13.

2.3.4.2. Thermal conductivity:

The thermal conductivity ($\kappa$) measurements were carried out in a closed-cycle refrigerator over temperatures from 10 to 300 K [184] using a direct heat-pulse method. A schematic diagram of the thermal transport setup is shown in figure 2.14.

![Schematic diagram of thermal transport setup](image)

**Fig.2.14. A schematic diagram of the thermal transport setup [184]**

The samples were cut to rectangular bars of dimensions $1.5 \times 1.5 \times 5.0$ (mm$^3$). One end of the sample was mounted on a copper block, which served as a heat source and a very small
calibrated chip resistor was set at the other end of the sample as a heat source. The temperature difference was measured by using a Type E (Chromel versus Constantan with 0.001” in diameter) differential thermocouple with the junctions thermally attached to two well-separated positions along the sample. To minimize the heat radiation the temperature difference was controlled to less than 1K. All measurements were performed on warming at a rate slower than 20 K/h. The absolute accuracy is about 20%, mainly due to the uncertainty on the dimensions of samples. The sample configuration of the thermal transport measurement is shown in figure 2.15.

Fig. 2.15. Sample configuration of thermal transport measurement [184]

2.3.4.3. Specific Heat:

It can be measured by various methods[185-186] like semi adiabatic method [187], relaxation calorimeter [188], AC calorimeter [189] and differential scanning calorimeter [184] etc. The classic definition of specific heat was used to perform specific measurements, i.e.

\[
C_p = \lim_{\Delta t \to 0} \left( \frac{dQ}{dT} \right)_p
\]

(2.8)

where \(dQ\) is a heat input that causes a small temperature rise \(dT\) in the sample. There are many techniques designed to measure specific heat, for example: adiabatic method, differential scanning calorimetry, heat-pulse relaxation method, ac method, and so on. At a given temperature, or on a slowly rising temperature ramp, a pulse of power is added to a
sample and the temperature variation is noted. This technique is called the adiabatic method, in which one uses a thermally isolated sample of large enough mass ($\approx$ 1g) and large enough contact area to minimize the effects of stray heat leaks. The advantage of this technique is that we can get an absolute adiabatic condition. By comparing with known specific heat of a standard sample, one can get the unknown specific heat of the measuring sample. This technique is called differential scanning calorimetry. By knowing the power applied to the sample accurately, and by knowing the response of the calorimeter either empty or when containing a standard, absolute measurement of $C$ with reasonable accuracy can be obtained. It is also possible to measure specific heat over a wide range of temperature (several hundred K) fairly quickly (several hours) by differential scanning techniques. Another technique appropriate for small sample calorimetry is heat – pulse relaxation method, or time constant method. By controlling a heat switch, one can input proper heat to a sample to arrive the temperature that has been set. The change of sample temperature is given by:

$$T = T_1 + \Delta T_0 \left(1 - e^{-\frac{T}{\tau}}\right)$$  \hspace{1cm} (2.9)

where $T_1$ is the bath temperature, $\Delta T_0$ is the maximum change of the sample temperature and $\tau$ is the internal time constant which the sample needs to get internal equilibrium. The relationship between specific heat $C$ and time constant $\tau$ is given by:

$$C = \tau \left(\frac{\Delta P}{\Delta T_0}\right)$$  \hspace{1cm} (2.10)

where $\Delta P$ is the heat power. This technique is essentially restricted to point to point measurement. However, the specific heat of sample is usually large at high temperature, it leads to large internal time constant, and it will take very long time to get just one data. Another disadvantage of this method is that, for small $C$, $\tau$ can be relatively short mandating some fast recording electronics, e.g., a signal average. In 1968, Sullivan and Seidel [189] published a landmark paper describing how to measure specific heat of small samples using an ac method using commercially available lock-in amplifiers. By passing an ac modulated light heat source through the sample, one can detect the small vibration of sample temperature by lock-in amplifier with high sensitivity, and the relative accuracy is about 0.1%. The disadvantage of this technique is that we can get only relative specific heat, because the power of the ac heat source is unknown.
In the present investigations, we have adopted the ac method calorimetry because of its great precision and also because of the fact that a small sample is needed (~μg). In addition, it provides a continuous readout of heat capacity as a function of various external parameters. Apparatus used in the present investigation- AC calorimeter setup for the measurement of specific heat is consisting of an AC calorimeter probe, a Dewar flask, Variable Temperature Insert (VTI), electronic instruments and personal computer is shown in figure 2.16.

![Diagram of AC calorimeter system](image)

**Fig.2.16. Schematic of the AC calorimeter system[184]**
In AC calorimeter setup there is superconducting magnet (NbTi) in the Dewar flask, and it provides maximum magnetic field 8 Tesla. The temperature controller (model ITC 503) is used to control the rate of the chamber temperature differences, the goal temperatures and the time needed for the chamber to maintain at a constant temperature by controlling the needle valve included in the VTI (Varied Temperature Insert). The DVM (digital voltmeter, model 182) is used to detect the electric potential differences $V_{DC}$ between the sample and thermal bath connected by a pair of thermocouples. Then transfer of $V_{DC}$ into the temperature difference can be made by known thermoelectric power of the thermocouple (type E) at different temperatures. The low noise transformer (model 1900) connected to another pair of the thermocouple is used to magnify the small signal $V_{AC}$ caused by the vibration of the sample temperature. The lock-in amplifier (model SR 830) is used to take the chopping frequency $f$ data and the ac signal data magnified by the transformer. All the data processing and controlling are performed by means of a computer through GPIB (IEEE – 488 bus). Finally, the heat capacity vs. temperature curve was displayed on the monitor. More details of the structure of the sample holder are provided in Fig. 2.17 and Fig. 2.18.

![Schematic of the ac calorimeter probe and connection between the electronic instruments](image-url)
Chapter 2  Electrical, magnetic and thermal properties of Bi doped RE$_{0.6}$-$_{3}$Sr$_{0.4}$MnO$_3$ and RE$_{0.7}$-$_{3}$Sr$_{0.3}$MnO$_3$ (RE=Pr, La) manganites

Experimental techniques

Fig. 2.18. The structure of sample holder[184]

a. Preparation before measurement

A spot welder was used to make thermocouple junctions and flattened the thermocouple to increase the contact area. The bases of the four junctions (Fig. 2.18) are sapphires that are adhered to the copper ring with dilute GE 7031 varnish. Both the sapphires and GE 7031 varnish have good thermal conductance, but are electric insulators. The sample was cut and sanded into proper size. Typical thickness of the sample is about 0.1mm.

b. Sample mounting

The mounting is adhered on the junction of two pairs of thermocouples by applying a little bit amount of glue. Four junctions are electrically conducting each other. After this, a PbS film was evaporated on the sample front surface. The sample holder was locked to the end of the ac calorimeter probe. The four enamel-insulated wires were welded to the four metallic pins on the annulus with tin solder. The chamber of the ac calorimeter was evacuated by mechanical pump. A little bit of helium gas was put as exchange gas and by adjusting the vacuum valve; the gas pressure of the probe can be maintained about 200m Torr.

c Parameters of the electronic instruments:

1. Function generator: A square wave output was used to drive the stepping motor.
2. Halogen lamb housing: One can adjust the four adjustments on the lamb housing
3. Lock-in amplifier (SR830)
4. Computer (Lab view software):
Lab view software is used for setting cooling or warming and adjusting the increment (0.05, 0.1 or 0.2 K/point).

The measuring processes are shown in Figure 2.19.

Fig.2.19. Flow chart of the specific-heat measurement