CHAPTER II

EXPERIMENTAL TECHNIQUES
2.1. SAMPLE PREPARATION: Since Bi-system is known to have three superconducting phases existing together, various techniques have been tried out to obtain an enhanced volume of high-$T_c$ (2223) phase. Different techniques are in practice for synthesizing these materials such as solid state reaction technique, diffusion process, chemical route etc. We have adopted the most common technique viz., solid state reaction technique for synthesizing a variety of specimens for present studies. In general, either oxides, carbonates or nitrates of the constituent metals are mixed thoroughly in appropriate proportions and ground well. The mixed powder is calcined for several hours at high temperatures ($\approx 800^\circ$C). Repeated calcination with intermediate grinding lead to homogeneous compound. The calcined powder is ground again, pressed in the form of pellets and sintered at $\approx 850^\circ$C for several hours and cooled down accordingly. Sintering provides the connectivity of the grains. We have synthesized a large number of specimens with different compositions. These are discussed below.

2.1.a. $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$: Appropriate amounts of $\text{Bi}_2\text{O}_3$, $\text{SrCO}_3$, $\text{CaCO}_3$ and $\text{CuO}$ powders, in molar ratio of $\text{Bi}:\text{Sr}:\text{Ca}:\text{Cu}:\text{O}=2:2:2:3$, are mixed thoroughly in a pestle-mortar, mixed powder is calcined at $840^\circ$C for 20 hr in air and quenched to room temperature. The calcination is repeated second time after regrinding the calcined mass. Calcined mass is ground and pressed in the form of circular pellets and rectangular bars.
(45X4X3 mm) at a pressure of 3000 psi using a hydraulic press. The final sintering is carried out for rectangular shaped specimens (45X4X3 mm) at 843°C for 90 hr and at 840°C for 34 hr respectively for two series (series I and II) of compounds. 5wt% and 7.5wt% of PbO (99.9% pure) are then added to the master compound I and II respectively and annealing is carried out at 500°C and 600°C from 2 to 18 hours in a vacuum of 10⁻¹ torr or in oxygen atmosphere.

2.1.b. SUBSTITUTION OF Bi BY Pb: Addition of Lead (Pb) is reported to enhance the volume fraction of high T_c phase in Bi-system. To get an optimum value of lead for stabilizing the 2223 phase, specimens are prepared by varying the concentration of Pb in composition Bi_{2-x}Pb_xSr_Ca_Cu_O_y. Specimens are prepared using the solid state technique. Bi_2O_3, PbO, SrCO_3, CaCO_3 and CuO are taken in the appropriate quantities. The mixed powder is calcined at 835°C for 12 hours in air and furnace cooled. The calcined mass is ground again, pelletized and sintered at 840°C for 36 hours. Final sintering is carried out at 845°C for 48 hours in air and furnace cooled to room temperature. Value of (x) is varied from 0 to 0.5.

2.1.c. CHANGE IN Sr CONCENTRATION: As Pb 0.3 and 0.4 gives the best specimens, only these two concentrations of Pb are used in later specimens. Specimens are prepared in two batches, one using SrCO_3 and other using Sr(NO_3)_2 as starting materials. Sr
concentration has been changed from 2 to 1.4 in steps of 0.2 in the composition \( \text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{x}\text{Ca}_{2}\text{Cu}_{3}\text{O}_{y} \). Powders of \( \text{Bi}_{2}\text{O}_{3}, \text{PbO}, \text{SrCO}_{3} \) or \( \text{Sr(NO}_{3}\text{)}_{2}, \text{CaCO}_{3} \) and \( \text{CuO} \) are taken in molar ratio of \( \text{Bi}:\text{Pb}:\text{Sr}:\text{Ca}:\text{Cu}=1.7:0.3:x:2:3 \). First sintering is carried out at a temperature of 815°C for 48 hr. Final sintering is carried out at temperatures 845°C and 850°C for 192 hr and 144 hr for specimens using \( \text{SrCO}_{3} \) and \( \text{Sr(NO}_{3}\text{)}_{2} \) respectively with intermediate grinding, sintering and then furnace cooled to room temperature. Furnace cooling takes about 10 hr starting at 850°C.

2.1.d. ANNEALING UNDER DIFFERENT CONDITIONS: To study the effect of different annealing atmospheres on the superconducting properties specimens are annealed in vacuum, air and oxygen. First, \( \text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_{1.6}\text{Ca}_{2}\text{Cu}_{3}\text{O}_{y} \) is prepared with the calcination at 835°C for 24 hr followed by grinding, pelletization, sintering at 840°C for 30 hr and then furnace cooled to room temperature. After grinding, four rectangular specimens of size 45X4X3 mm are made out of the powdered mass and sintered at 840°C for 30 hr and furnace cooled. One of the pellets is annealed in vacuum at 550°C for 4 hr under rough vacuum \((10^{-1} \text{torr})\), in air and in oxygen atmosphere respectively. Specimen 1 is without annealing at 550°C.

2.1.e. DOPED SPECIMENS: We have studied the effect of Sb and Li doping in \( \text{Bi(Pb)SrCaCuO} \) compounds. These specimens are prepared in two different batches.
(i) **Li-Doping:** Different compounds of the formula $\text{Bi}_{1.6} \text{Pb}_{(0.4-x)} \text{Li}_x \text{Sr}_{1.6} \text{Ca}_2 \text{Cu}_3 \text{O}_y$ have been prepared where $x$ varies from 0 to 0.3. $\text{Bi}_2\text{O}_3$, $\text{PbO}$, $\text{Li}_2\text{O}_3$, $\text{SrCO}_3$, $\text{CaCO}_3$ and $\text{CuO}$ are used as initial materials, these powders are taken in appropriate molar ratio and mixed throughly. Mixed powders are calcined at 820°C for 140 hr. Calcined material is ground and pressed in the form of rectangular bars and sintered at 840°C for 72 hr followed by final sintering at 845°C for 72 hr.

(ii) **Sb-Doping:** $\text{Sb}_2\text{O}_5$ is used as initial material for Sb doped specimens. $\text{Bi}_{1.6} \text{Pb}_{(0.4-x)} \text{Sb}_x \text{Sr}_{1.6} \text{Ca}_2 \text{Cu}_3 \text{O}_y$ are prepared with different values of $x$ (ranging from 0 to 0.2). Method of preparation is same as discussed before except the heat treatment and duration of sintering. Sintering is carried out for 72 hr at 840°C and 850°C respectively and then furnace cooled to room temperature.

2.1.**f. SILVER ADDITION TO BPSCCO:** Ag addition lowers the melting point of the composition. The formation of the high $T_c$ phase requires a precise control of the temperature. To avoid the problem of phase segregation or formation of 2223 phase in small amount, Ag is added to the preformed material. First pure BPSCCO ($\text{Bi}_{1.6} \text{Pb}_{0.4} \text{Sr}_{1.6} \text{Ca}_2 \text{Cu}_3 \text{O}_y$) is prepared using usual solid state reaction method with initial calcination at 835°C for 24 hr. Second calcination is carried out at 840°C for 48 hr. The calcined powder is ground and five bar shaped (45X4X3
mm) specimens are prepared by using this pure calcined powder as well as after mixing it with varying amounts of AgNO₃ corresponding to a silver ratio of 5, 10, 20 and 50% by weight. All the specimens are sintered at 810°C for 24 hours and furnace cooled to room temperature.

2.2. CHARACTERIZATION: Bi-system is a multi phase system, it is very necessary to characterize it before going for any further studies. The transport properties are in particular very sensitive to impurities and imperfections. Characterization is carried out by using X-Ray diffraction (XRD) and scanning electron microscope (SEM). Room temperature XRD patterns are taken on Siemens D-500 diffractometer using CuKα radiation in 2θ range of 3° to 50° (mostly on powdered specimens but sometimes on pellets as such) and indexed for hkl values corresponding to different phases.

SEM micrographs are taken on JEOL 35CF scanning electron microscope on the fractured surface of the specimen to study the grain structure of the specimens.

2.3. MEASUREMENT TECHNIQUES: Before going for any measurement, specimens are checked for Meissener effect by floating a magnet over the specimen cooled to liquid nitrogen (LN₂). Two basic measurements are carried out for most of the specimens, resistance and thermoelectric power (TEP) variation with
temperature. Most of the specimens are superconducting at temperatures well above the LN$_2$ (77.4K) temperature. Most of the measurements are restricted to the temperature range of 78K to 300K but in some cases TEP measurements are carried out even at lower temperatures by pumping over the liquid nitrogen bath.

2.3.a.RESISTANCE MEASUREMENT: Electrical resistance of the specimens is measured in a variable temperature cryostat from room temperature to LN$_2$ temperature with a temperature interval of about 5 Kelvin at high temperatures and 2 Kelvin at low temperatures. A four probe method is used for measuring the electrical resistance. A Copper-Constantan thermocouple is used for measuring the temperature of the specimen. One thermocouple junction is kept in good thermal contact with specimen and the other junction at LN$_2$ temperature. Silver-paste is used for making current and voltage contacts. A Keithley constant current source (model 224) is used for supplying constant current to the specimen and a Keithley nanovoltmeter (model 181) is used for measuring the voltage drop across the specimen. Measuring current is kept constant generally at 1mA. Voltage is measured after reversing the direction of the current at each temperature and taking the average of the two voltages (to avoid the effect of stray thermo e.m.f.in the measured resistance).

2.3.b.TEP-MEASUREMENTS: Thermoelectric power can be measured in
two different ways

(i) Integral Method

(ii) Incremental (Differential) Method

We have used Incremental method for measurement of TEP. Block Diagram of the TEP set up is shown in Fig. 2.1. Basic principle of measurement is the following: if there is a temperature gradient \( \Delta T \), then a voltage gradient \( \Delta V \) will be generated (Seebeck Effect) and ratio of voltage gradient to temperature gradient is thermoelectric power. While using this method \( \Delta T \) should be small so that absolute properties at two temperature of the specimen should not change in that interval, at the same
time $\Delta T$ should be large enough to generate a voltage gradient which can be measured accurately. Rectangular specimens are used for TEP measurement. The specimen is mounted inside a vacuum can made of brass (size 40mm dia. and 80 mm height). A heater is mounted on the lower end of the specimen and upper end is fixed in good thermal contact to the copper plug welded to the lid of brass vacuum can. Inside the can rough vacuum is maintained (of the order of $10^{-1}$ torr). Lid of the brass can is soldered to a stainless steel tube which is connected to the pump line. All the leads are taken out through a SS tube connected to the can and are vacuum sealed at the top using a Apezone black-wax. At two points of the specimen about 15mm apart two voltage leads are connected which are in good electrical contact to the specimen to measure $\Delta V$. Silver paste is used for voltage contact. Cu leads are used to monitor $\Delta V$. A differential thermocouple is used for measuring $\Delta T$ at the same points where $\Delta V$ is measured. A copper-constantan thermocouple is attached to the upper point for measuring the sample temperature $T_{\text{cold}'}$, the absolute temperature is taken as $T_{\text{cold}'} + \frac{\Delta T}{2}$.

The vacuum can is sealed with Wood’s metal solder (Wood’s metal melting temperature is quite low about 55°C). For a measurement of TEP on each specimen, the can has to be sold-ered and resoldered every time using Wood’s metal. Vacuum is maintained inside the can to minimize the heat losses from specimen so that a steady $\Delta T$ along the specimen is attained quickly. The
can is placed in a LN$_2$ cryostat where temperature is lowered slowly. A temperature gradient of about 1-2K is maintained in the whole temperature range of measurement. Data points are taken at a difference of about 3-4K at high temperature range and still closer at low temperature range. Measured thermo-electric power is corrected by subtracting out the TEP of the copper leads. The cryostat has facility for pumping by which one can go to a temperature of about 71K. Generally for one set of measurement, 8-9 hr is required for complete data acquisition.

Results of these measurements are given in Chapters III, IV and V.