CHAPTER II

EXPERIMENTAL METHODS

This chapter describes the experimental methods employed for the preparation and characterisation of different materials used in the present study.

II.1 Processing of YBa$_2$Cu$_3$O$_{7-δ}$ Superconductors

The YBa$_2$Cu$_3$O$_{7-δ}$ [YBCO] ceramic superconducting compounds were prepared by the conventional solid state reaction method. Solid state reaction or powder metallurgy is a commonly adopted synthesis route for producing multicomponent oxides(1). This method employs a series of mixing, grinding and heating cycles with varying temperatures and time of heating schedules. Appropriate amount of ytttrium oxides, barium carbonates and copper oxides or copper nitrates were weighed and mixed in the stoichiometric ratios in an agate mortar. The mixture was then subjected to calcination which promotes the decomposition of carbonates, nitrates or other impurity phases, leading to the formation of the desired phase of the superconducting YBCO
compound. The calcined powder so obtained was ground well and pressed in the form of pellets and sintered at high temperatures. Sintering is one of the most important means in powder metallurgy to develop the microstructure by the reduction in grain boundary volume and increase in particle contact region.

II.2 Processing of REBa₂HfO₅.₅ [RE = Y, Gd, Sm] Ceramic Substrates

Rare-earth barium hafnates [REBa₂HfO₅.₅] were prepared by the conventional solid state reaction method. Rare earth oxides [Y₂O₃, Gd₂O₃, or Sm₂O₃], barium carbonates [BaCO₃] and hafnium oxides [HfO₂] were taken in the stoichiometric ratio and were mixed thoroughly in an agate mortar. The mixture was then subjected to calcination followed by sintering. The calcination and sintering temperature and duration of heating were different for different materials and are described in detail in the respective sections.

II.3 Experimental Set up for the Fabrication of YBa₂Cu₃O₇δ Thick Films

Thick films are complex non-equilibrium systems having physical properties that are intimately related to their microstructure which in turn is determined by the combination of material properties and processing conditions. The term thick film comes from the fact that the films deposited are relatively thicker [1-100 μm] in comparison with those obtained from
vacuum deposition techniques (4). In the present work screen printing and dip coating techniques were used for the fabrication of YBCO and YBCO-Ag composite thick films.

II.3.1 Screen Printing

Screen printing is one of the techniques which is being widely used in industry for the fabrication of thick films (5). Ink containing the desired material is forced through the openings of a screen by a squeegee which traverses the pattern and gets printed onto a substrate. Patterns of electronic and microwave circuits and other devices can be directly printed by this method. The essential components required for screen printing are the fine powder of the desired material, the organic solvents for making ink, substrates, screen mesh containing the desired pattern and a squeegee for applying the ink. In the present work mesh size of 325 was used for screen printing superconducting films. Schematic diagram of the experimental set up for screen printing used in the present study is given in Fig.II.1.

II.3.2 Dip-coating

Dip-coating technique is found to be a relatively simple and reliable method for the fabrication of superconducting YBCO thick film of thickness $< 5 \mu m$. Highly polished substrates are dipped into the suspension containing the desired material and then dried immediately. The thickness of the films
Fig II.1  Schematic diagram of screen printing apparatus
can be controlled by the repetitions in dipping the substrates in the suspensions(6). Films can be coated on large area, on both sides of the substrates, on any irregular surface, cylindrical substrates or spherical substrates, by making use of dip-coating technique. High quality superconducting films with uniform surface and thickness as low as 2 μm can be prepared by this technique.

II.4 X-ray Powder Diffraction Technique

A Rigaku D MAXC [Japan] computerised x-ray diffractometer with nickel filtered Cu-K\textsubscript{a} radiations [\(\lambda = 1.5406 \text{ Å}\)] was used for the structural characterisation of different materials prepared during the present study. The incident Cu-K\textsubscript{a} radiations of x-rays gets diffracted according to Bragg's law from the crystallites of the finely powdered samples kept in the specimen holder. The diffracted rays go out from the individual crystallites which happen to be oriented with planes making an incident angle with the beam satisfying Bragg's equation \(n\lambda = 2d\sin\theta\) where \(\lambda\) - is the wavelength of the incident radiation and \(d\) - is the interplanar spacing (7). X-rays are normally produced by bombarding a metal target like Cu, Mo or Co with a beam of electrons emitted from a heated filament. Debey-Scherrer method was used for x-ray analysis and the schematic diagram of the method is shown in Fig.II.2. In the Rigaku x-ray diffractometer the reflection peaks are recorded by a computer with slow scanning speed and the diffractograms were plotted by the plotter.
Fig.II.2. Schematic diagram for the Debye Scherrer x-ray powder method
attached to it. From the computerised x-ray diffraction data the lattice parameters were calculated using the least square method(8).

II.5 Scanning Electron Microscope

Scanning electron microscope [SEM] is a powerful tool for the accurate observation of morphology, grain size and surface properties of materials. SEM consists of a vacuum system, a sample chamber, detectors, electron gun and a high resolution cathode ray tube. The kinetic energy acquired by electrons in an electron column, when they are accelerated through an electric field, is transferred to the sample and its dissipation yields a variety of signals available for analysis. The primary electrons interact with the electrons of the sample. These electrons have kinetic energy below 50 eV. Since they have very low energy, secondary electrons can escape from the sample only if they are created near the surface. Hence secondary electrons created at the topographic hills have a greater chance of escaping than those created at the topographic dales. Thus they are sensitive to the surface topography of the sample. Secondary electrons carry very little information regarding the elemental composition of the sample. However their topographic sensitivity
and higher spatial resolution makes them the most frequent choice for micrographic images. The SEM is most commonly used to provide images of high spatial resolution, usually using secondary electron signals. The image displayed on the Cathode Ray Tube is created by scanning the focused electron beam across some area of the sample while synchronously scanning an analogous pattern on the Cathode Ray Tube. The brightness of the Cathode Ray Tube is modulated on the basis of the intensity of the signal of interest.

During the course of the present work, scanning electron microscope JEOL JSM 35C was used. The electron gun was operated at an electron energy of 15-25 KeV with a beam diameter of 20-25 nm. The unit is operated at 1 KV and 10 mA current. The surface of the samples to be observed was coated with gold [about 100Å thickness in the case of insulator samples] by sputtering technique to avoid sparking during SEM study. Gold coating is not necessary in the case of superconducting samples. The samples were then mounted in the chamber of electron microscope and the system was evacuated to 10⁻⁶ torr pressure. The electron beam was focused on selected areas of the samples according to the requirements and at different magnification.
II.6 Electrical Measurements

In the present work, the electrical properties of the superconducting samples were studied using temperature-resistivity and critical current density measurements by d-c four probe method.

II.6.1 Resistivity and Critical Temperature Measurements - Vander-pauw Method

The resistivity of the superconducting pellets were measured by d-c four probe method in Vander-pauw geometry instead of the usual two probe method to avoid lead resistance. In order to measure the resistivity of a flat lamella of any shape, any four point contacts say A, B, C and D at arbitrary regions are to be considered. The schematic diagram is shown in fig. II.3.

Fig. II.3. A flat lamella of arbitrary shape with four contacts on the periphery and used in the Vander Pauw's method for resistivity measurements.
A current $I_{AB}$ is applied to contact A and taken off at contact B. The potential difference across CD is measured as $V_D - V_C$.

Thus

$$R_{AB,CD} = \frac{V_D - V_C}{I_{AB}}$$

and

$$R_{BC,DA} = \frac{V_A - V_D}{I_{BC}}$$

A simple relation exists between $R_{AB,CD}$ and $R_{BC,DA}$ and is

$$\exp\left[\frac{\pi d}{\rho} R_{AB,CD}\right] + \exp\left[-\frac{\pi d}{\rho} R_{BC,DA}\right] = 1 \quad \text{[1]}$$

where 'd' is the thickness of the sample and 'ρ' its resistivity. The solution of this equation gives the value of resistivity of the sample.

$$\rho = \frac{f \pi d}{\ln 2} \frac{R_{AB,CD} + R_{BC,DA}}{2} \quad \text{[2]}$$

where 'f' is a factor which is a function of the ratio $\frac{R_{AB,CD}}{R_{BC,DA}}$ as plotted in Fig. II.4.

Fig. II.4. Graph showing $f$ versus $\frac{R_{AB,CD}}{R_{BC,DA}}$.
For calculating $\rho$ from equation [2], $R_{\text{AB,CD}}$ has to be calculated and then obtain the value of 'f' from Fig.II.4.

The specimen for the resistivity measurement was mounted on a copper plate at one end of a long copper tube, isolated from it by a thin layer of insulating varnish. Four point contacts were given on the periphery of the specimen sample using conducting silver paste. Four copper leads were attached to these contacts. A calibrated copper-constantan thermocouple was fixed to the copper strip very close to the sample. The leads from the contacts as well as the thermocouple were anchored to the large copper tube and taken out at the other end of the tube. The sample holder set up was introduced into a cylindrical brass vessel and was firmly fixed at the top of the brass vessel in such a way that it did not touch the sides or bottom of the brass vessel. The closure at the top was made air tight. The brass vessel was evacuated and a small amount of nitrogen gas was introduced. The whole arrangement was then introduced into a liquid nitrogen Dewar. The experiment was done by allowing the sample to cool continuously at a very slow rate, and taking the readings at close intervals. The rate of cooling was controlled by introducing appropriate amount of nitrogen into the brass vessel as well as by raising the dewar smoothly and slowly by using a lab jack. The schematic diagram of the sample holder set up used in the present study is shown in Fig. II.5.

A constant current [say 1-10 mA] was passed through the sample between
Fig II.5 Sample holder set up to measure the electrical resistivity of the samples.
the point contacts A and B by a Keithley model 220 programmable constant current source. The voltage drop was measured between C and D for a given current using a Keithley model 181 nanovolmeter. The current was then reversed between A and B and the voltage drop was measured in order to check the accuracy. The same current was then applied through the sample between B and C and the corresponding voltage drop was measured between A and D. At the superconducting transition temperature the voltage drop across the two point contacts was found to be zero.

II.6.2 Critical Current Density Measurements

The critical current density ($J_c$) of superconducting YBCO thick films was measured at 77K in zero magnetic field by four probe method following $1 \mu V/cm$ criterion. Thick films in the form of rectangular shape having 10 mm length, 20 mm width and $\sim 10 \mu m$ thickness [for screen printed film], and $\sim 3 \mu m$ thickness [for dip coated film] were used for the $J_c$ measurements. The schematic diagram for the critical current density measurement set up is shown in Fig. II.6.

![Schematic diagram for the critical current density measurements](image)

Fig. II.6. Schematic diagram for the critical current density measurements.
Four point contacts using palladium paste were given linearly, with two contacts at the ends [A & B] of the film to pass the current from a d-c current source and other two contacts C and D [2.5 mm apart] at the middle of the film for measuring the voltage [V] developed across the film due to the current along its length. The current-voltage relations are measured at 77K. For measuring the current density, a particular current from the battery is passed through the film. At 77K the voltmeter shows zero voltage. As the current increases above a certain limit a voltage drop can be observed. Hence the current density can be calculated.

II.7 Measurement of Dielectric Properties

The dielectric properties of ceramic substrate samples were measured using an HP4192A Complex Impedance Analyser in the frequency range 30 Hz to 13 MHz at room temperature and at liquid nitrogen temperature. The dielectric constant [ε'] and dielectric loss factor [tanδ] of the polished samples in the form of circular pellets were measured using silver electrodes on both sides of the discs. The capacitance and dissipation factor were directly measured as a function of frequency.

A dielectric is characterised by the complex permittivity or dielectric constant and the dielectric susceptibility. The permittivity is dependant on the frequency of the applied field and is associated with power absorption,
proportional to the imaginary part of the permittivity. The dissipation of energy within the dielectric of a capacitor can be described [for an alternating current of particular frequency] in terms of the tangent to its loss angle 'δ'. The frequency dependant 'tanδ' is equal to the ratio of the imaginary and real parts of the permittivity. If the dielectric medium is loss free [perfect dielectric] then tan δ = 0. The dielectric constant of the dielectric samples were calculated from the values of capacitance using the formula

\[ C = \frac{\varepsilon' \varepsilon_0 A}{d} \]

where \( \varepsilon' \) is the dielectric constant, \( \varepsilon_0 \) is the permittivity of the free space, 'd' is the thickness of the sample and 'A' is the area of the disc.
References