CHAPTER II

PREPARATION AND CHARACTERIZATION TECHNIQUES

2.1 Introduction

Powder synthesis is one of the major challenges in the development of advanced ceramic materials for their various functional and structural applications. Ceramic industry requires the raw materials as powders and the quality of these powders has the strongest influence on the structure and properties of the final ceramic product. The processing of ceramics, both substrates and high Tc superconductors, involves preparation of high purity powders as single-phase materials (calcination), compaction of the single-phase powder into the desired shape followed by densification and texturing at high temperatures (sintering). The microstructure and the final properties of ceramic powders are largely depend on the characteristics of the starting powders such as the particle size and size distribution, particle shape and shape distribution, degree of particle agglomeration, chemical composition and homogeneity [1, 2]. A brief description of the various methods used for preparation of samples and different techniques used for their characterization are given in this chapter. However, the specific details regarding the sample preparation and characterization are described in detail in the respective chapters.

2.2 Ceramic Processing

The conventional way of advanced ceramic fabrication includes the powder preparation, shaping and sintering.
2.2.1 Powder Preparation:

In general the powder preparation technique fall in to three categories, viz., solid phase synthesis, liquid phase synthesis and gas phase synthesis. The solid phase synthesis (solid state reaction method) of ceramic oxides employs a series of mixing, grinding and heating cycles with varying heating schedule. In this method, the stoichiometric amount of the initial reaction mixture is calcined in a certain range of temperature for certain time. Calcination processes are endothermic decomposition reactions in which an oxysalt such as a carbonate, oxide or a hydroxide decomposes, leaving an oxide as a solid product and liberating a gas [3]. Solid state reaction is a relatively cheap technique for the production of ceramic oxide powders. The solid state reaction method, though widely used because of its simplicity, has certain disadvantages. In the case of multicomponent system, the mixing of the constituent salts or compounds is a very important part in solid state reaction method and one of the problems associated with the conventional mixing is that it may not result in sufficient transport of powders which in turn may prevent a complete solid state reaction during calcination. In the ball milled powders it is difficult to obtain reproducible uniform distribution of materials especially when one constituent fraction is present in small amounts. Inadequate mixing of powders can lead to compositional inhomogeneities, insufficient stoichiometry control and formation of extraneous phases during high temperature annealing. The presence of aggregates/agglomerates in calcined materials would result in high porosity and microstructural coarsening leading to poor sinterability and inferior physical characteristics [4-6].

In the present study, ceramic materials were synthesized by both solid state route and combustion process. In the solid state route, stoichiometric amounts of the reagents, which are oxides and/or carbonates, were thoroughly mixed in an
agate mortar with acetone as wetting medium for 2 h. The powders were dried in electric oven at 150°C for 2 to 4 h. The dried mixture was calcined in air at a desired temperature for ~ 24 h in alumina/platinum crucibles with multiple grindings. The resulting powder was ground well and the calcination step was repeated 2 to 3 times. In the present work ceramics materials were also synthesized as phase pure nanoparticles by using a modified combustion process. In this route aqueous solution of the constituent ions were prepared by dissolving stoichiometric amounts of respective nitrates/oxychloride/oxydes. These solutions were mixed together and an equivalent quantity of citric acid was added. The amount of citric acid was kept at the citric acid to cation ratio unity. The oxidant/fuel ratio of the system was adjusted by the addition of ammonium hydroxide and nitric acid. The solution containing the complex precursor at neutral pH was then heated in a hot plate. Initially the solution boils and on completion of evaporation the solution turns into a foam. The foam then ignites and the product of combustion was voluminous and fluffy.

2.2.2 Shaping

Depending on the shape and required characteristics, numerous powder forming process have been developed. The most commonly used powder shaping techniques are die pressing, rubber mold pressing, extrusion molding, slip casting and injection molding [6]. The powder itself consists of solid brittle particles, so it is difficult to fill the powder in a die by pressure alone. As the pressure is increased, there is more strain on the compact, and cracks that can cause the compact to fracture are formed. Therefore, a binder is usually added to enhance the fluidity of the powder [5]. Polyvinyl alcohol is the commonly used binder for the forming of oxide ceramics. In the present study, the powders were pressed uniaxially pressed at a pressure of ~ 350 MPa using a hydraulic press.
2.2.3 Sintering

Sintering is the most important step during ceramic processing because it is at this stage that a powder compact is exposed to the maximum temperature. When a ceramic material is heated, there is a certain temperature at which they begin to diffuse, and in most cases there is shrinkage resulting in densification. During this process, the redistribution of matter takes place in such a way that minimize the system free energy. Besides densification, many electrical, magnetic, optical and mechanical properties are determined by the physical and chemical changes during sintering at high temperature. Characteristics of the starting powder such as particle size distribution, degree of particle agglomeration, particle shape, shape distribution, particle aggregates, have a profound influence on densification and microstructural development [7]. A large number of sintering methods such as standard pressure sintering, hot pressing, hot isostatic pressing, reaction sintering, recrystallization sintering, ultra high pressure sintering are frequently employed [6]. In the present study, the sintering of the powder compacts were done in a programmable furnace in a certain temperature range.

2.3 Preparation of High Tc Superconducting thick films

A number of techniques has been proposed and are in use for the development of superconducting thick films. They include dip-coating, screen printing, spray pyrolysis, spin-coating, pain-on etc. All these techniques, in general, start with the preparation of a homogeneous mixture, known as ink, consisting of the superconductor powder and an organic vehicle. The vehicle is a mixture of polymers and solvents. The ink is then coated on the substrate by any of the above techniques and dried. The coated and subsequently dried coating are
fired at high temperature in order to sinter the particles in the ink so that a textured film is obtained.

In the present study, thick films of YBCO, Bi (2212) and Bi (2223) materials have been produced by dip-coating and melt texturing technique. For dip-coating, a suspension of the superconducting material was prepared by thoroughly mixing fine powders of the superconductor with isopropyl alcohol or n-butanol. For obtaining the film, the polished and cleaned substrate is dipped in the thick film suspension and the dipping process is repeated until a required thickness is achieved. The resulting film is then dried in a hot air oven and is subjected to controlled heat treatment. The actual temperature, time of annealing, rate of heating and cooling are described in the respective chapters.

2.4 Characterization techniques

The newly developed ceramic materials are crystalline and are dielectrics in nature. The structures of the materials are studied by x-ray diffraction technique and their dielectric properties are studied using an impedance analyzer. The nanoparticulate powders of the newly developed materials were characterized by differential thermal analysis, thermogravimetric analysis, FT-IR spectroscopy, BET surface area measurements, gas adsorption studies, agglomerate size analysis and high-resolution transmission electron microscopy in addition to powder x-ray and electron diffraction. Thermal analyses were also carried out on the coarse grained powders produced through the conventional solid state route. The superconducting properties of the superconductor-insulator composites and high Tc superconducting thick films were carried out by temperature-resistance measurements using four-probe technique.
2.4.1. Powder X-ray Diffraction Technique

Powder x-ray diffraction is one of the most important tools for the investigation of the structure of matter. This technique had its beginning in 1912 when Von Laue discovered that the crystal diffract x-rays in the same way as the visible light is diffracted by a diffraction grating. In other words, the crystal acts as a three-dimensional grating for the x-rays and the manner of the diffraction revealing the crystal structure of the matter. Later on, other uses were developed and today the method is applied, not only to the structure determination, but such diverse problems as chemical analysis, stress measurement, study of phase equilibria, measurement of particle size, determination of the orientation of one crystal or the ensemble of orientation in a polycrystalline aggregate [8,9].

The resolving power of any optical instrument limited to diffraction is proportional to the wavelength of the electromagnetic radiation used and the diffraction pattern are produced when the wavelength is comparable to the interatomic spacings in crystals. Radiations of longer wavelength are no longer diffracted by the periodic lattice of the crystal and that of shorter wavelength is diffracted through inconveniently smaller angles. x-rays have wavelengths comparable with the interatomic spacings in crystals. When x-rays of wavelengths comparable or smaller than the lattice constants are allowed to incident on a crystal, one or more diffracted beams are observed in directions quite different from that of incident beam. W. L. Bragg explained the observed angles of diffracted x-rays from a crystal in which the incident waves are reflected specularly from parallel planes of atoms in the crystal, with each plane reflecting the very small fraction of the radiation.
The diffraction of x-rays by the periodic structure of the crystal lattice is illustrated in figure 2.1. The horizontal dotted lines represent a parallel crystal plane with Miller indices (hkl) and W1W2 and W3W4 are the wave fronts incident and scattered by the periodic lattice of the crystal. The scattered waves undergo a constructive interference when

\[ 2d_{hkl} \sin \theta = n\lambda \]  

(1)

where \( d_{hkl} \) is the spacing between crystal planes, \( n \) is the order of the spectrum and \( \lambda \) is the wave length.

![Diagram of x-ray diffraction](image)

**Figure 2.1:** Reflection of a plane wave by a set of parallel planes.

For the present study, the powder X-ray diffraction (XRD) patterns were obtained using a computerized Rigaku Dmax (Japan) diffractometer employing Nickel filtered CuK\( \alpha \) radiation (\( \lambda =1.5406 \) Å). The XRD patterns were recorded at a scan speed of 4°/min at a step scan of 0.01°. Identification of the phases is done by comparing the d spacings and line strengths of the observed x-ray diffraction
pattern of the sample with standard reference data. The samples for x-ray diffractograms were prepared by smearing the finely ground powder on a standard glass plate provided with a groove.

2.4.2 Differential Thermal Analysis (DTA):

Differential thermal analysis is concerned with the detection of physical or chemical changes, which may occur when matter is heated. Specifically, DTA studies the change in absorption or liberation of heat by a sample measured as a function of the temperature. This change is compared to a reference substance that has been submitted to the same conditions. The method is especially suited for studying the structural changes within a solid at elevated temperatures and is mostly qualitative. For the present study, Differential thermal analysis was carried out using a Shimadzu DTA-50H unit with alumina as reference material. The samples were heated in nitrogen atmosphere at a heating rate of 10°C/min from room temperature to 1300°C. ~20-mg powder is used for each measurement.

2.4.3 Thermogravimetric Analysis (TGA)

Thermogravimetry studies the weight changes takesplace in a sample as the temperature is gradually raised in a certain rate. Two modes are commonly employed for thermogravimetric analysis. The first type, dynamic thermogravimetry subjects a sample to a continuous increase in temperature, usually linear with time. The second type, isothermal thermogravimetry subjects a sample to a constant temperature for a long time and the weight changes is noted. The instrument used is an automatic thermobalance. Information gained from TGA is often enhanced by the application of DTA, as the two techniques are complementary. The combination of TGA with the information from X-ray
diffraction and DTA yields a good quantitative estimation of solid state reaction. For the present study, thermogravimetric analysis was carried out using a Shimadzu TGA-50 unit at a heating rate of 10°C/min in nitrogen atmosphere from room temperature to 1100°C, ~5 mg powder is used for each measurement.

2.4.4. IR spectroscopy

The principle of this technique lies in the fact that when IR interacts with the materials, various chemical bonds in the material vibrate as it absorbs the IR radiation. These vibrations are either in the stretching or in the bending mode. When infrared light is passed through a material some of the frequencies are absorbed while other frequencies are transmitted through the sample without being absorbed. FT-IR spectra were recorded using a Nicolet 1 400D FT-IR spectrometer. The materials were finely dispersed in KBr using an agate mortar and pestle. The finely dispersed material was then pressed in the form of circular discs of ~10 mm diameter and 0.5 mm thickness at a pressure 250 MPa. These pellets were then dried with IR light before the FT-IR spectrum has been recorded.

2.4.5 Gas Adsorption Technique

Analysing the surface character of powder is perhaps one of the most important and most difficult procedures in ceramics characterization. Surface phenomena are a consequence of asymmetrical or unbalanced forces between atoms and molecules at the interface of a particle and are electronic in origin. The direct means of the characterization of the surface of ceramic powder is the transmission electron microscopy and will be described later. The indirect methods include (i) interaction of the powder with a liquid and (ii) interaction of the powder with a gas.
One of the most popular techniques used for the determination of the specific surface area of fine powders is that of low temperature nitrogen gas adsorption. What is measured is the amount of nitrogen gas adsorbed by a powder sample at liquid nitrogen temperatures over a range of gas partial pressures. The amount of gas forming a monolayer of the powder surface is usually calculated using Brunauer, Emmet and Teller (BET) equation [10].

\[
\frac{P}{V(P_0 - P)} = \frac{1}{V_mC} + \frac{C-1}{V_mC} \frac{P}{P_0}
\]

(2)

Where \( V \) is the total volume of gas adsorbed, \( V_m \) is the gas adsorbed when the adsorbent surface is covered with a unimolecular layer, \( P \) is the equilibrium pressure of the system, \( P_0 \) is the saturation pressure of the adsorbate gas, \( C \) is a constant dependent on the heat of adsorption and heat of liquefaction of the adsorbate gas, is in the range 50 to 300 for many adsorbents[11].

It has been shown that for \( P/P_0 \) values 0.05 to 0.30, the plot of \( [P/V (P_0 - P)] \) versus \( P/P_0 \) is a straight line having a slop of \( (C-1 / V_mC) \) and an intercept of \( 1/V_mC \) making it possible to calculate both \( V_m \) and \( C \). The specific surface area of the powder is obtained from the relationship

\[
S = \frac{V_m\sigma N}{V_oW}
\]

(3)

Where \( \sigma \) is the area occupied by one molecule of adsorbate (assumed 16.2 \( \text{Å}^2 \) for nitrogen at 77 K), \( N \) is the Avagadro’s number, \( W \) is the weight of the powder sample and \( V_o \) is the ideal gas volume [12].

The average particle size of the powder was calculated from surface area values by assuming they all consists of monosized hard spherical particles. The particle size is given by [12].
Where \( p \) is the density of the material and \( S \) is the specific surface area.

In the present study, the ceramic powders were degassed at 200°C for 24 h using an electric oven and the nitrogen gas adsorption studies were carried out in a Micromeritics unit model Gemini 2360. For generating adsorption isotherm, relative gas pressure is increased in different steps and the volume of the nitrogen gas adsorbed for 30 min was measured. The gas adsorption studies were done at liquid nitrogen temperature.

2.4.6 Agglomerate size Analysis

Agglomerate size distributions of the powders were studied using sedimentation technique. The usefulness of the sedimentation technique for agglomerate size measurement relies on the fact that the rate of fall of a particle in a fluid medium is proportional to the volume of the particle [12]. The rate of fall (\( v \)) of a spherical particle is related to the diameter (\( d \)) of the particle by

\[
d = \frac{6}{\rho \delta}
\]

(4)

Where \( \rho \) is the density of the material and \( \delta \) is the specific surface area.

\[
d = \left( \frac{18 \eta \cdot v}{(\rho - \sigma)g} \right)^{1/2}
\]

(5)

where \( \eta \) is the viscosity of the fluid, \( v \) is the rate of fall (terminal velocity), \( \rho \) is the particle density, \( \sigma \) is the fluid density and \( g \) is the acceleration due to gravity.

For the present study, the agglomerate size distribution of the powders were studied by using a Micromeritics sedigraph model 5700. The powders were ultrasonically dispersed in water before the agglomerate distribution curve was recorded.
2.4.7 Transmission Electron Microscopy

Transmission electron microscopy is the tool for the *in situ* measurement of powder surfaces. The wave nature of moving electrons is the basis of the electron microscope. The wavelength of electron wave is equal to

\[
\lambda = \frac{12.26}{\sqrt{V}} \text{ Å}
\]  

(6)

Where \(V\) is the accelerating voltage.

The resolving power of any optical instrument, which is limited by diffraction, is proportional to the wavelength of whatever is used to illuminate the specimen. In the case of a good microscope that uses visible light, maximum useful magnification is about 500X, higher magnification gives larger images but do not reveal any more details. However fast electrons have wavelengths very much shorter than those of visible light and are easily controlled by electric and magnetic fields because of their charge. This diffraction of electron beams is the principle of a Transmission Electron Microscope.

In transmission electron microscopy, electrons of higher energy (\(\sim 10^5\) eV) are allowed to transmit through the specimen surface. Some electrons will be transmitted and some will be diffracted by the specimen as the electron beam strikes it. If the transmitted beam is used for the generation of micrographs, such pictures are called bright field micrographs. In dark field mode, the diffracted electrons are used for the generation of micrographs. Both in bright and dark field images, particles with same orientation have the same gray level. The selected area electron diffraction patterns can also be utilized for the study of crystal structure. The geometry of indexing the electron diffraction pattern is shown in fig.2.2 [13].
Figure 2.2: The Geometry for Indexing an Electron Diffraction pattern

Where, $K_o$ is the direct wave vector \((2\pi / \lambda)\), $K$ is the diffracted wave vector, $G$ is the diffracted lattice vector \((2\pi / d)\), $L$ is the camera length, $R$ is Radius vector of the ring (spot).

From the geometry of triangles

\[
\frac{k}{G} = \frac{L}{R} \Rightarrow d = \frac{L\lambda}{R} \tag{7}
\]

Therefore by knowing the camera length, wavelength of electron wave and radius of the ring or spot, structure of the material can be elucidated.

In the present study the morphology and structure of the materials were studied by a JEOL 2000 EXII High Resolution Transmission Electron Microscope (HRTEM) operated at 200kV and at a vacuum of $10^{-6}$ Torr. The powder particles were supported on a carbon film coated on a 3 mm diameter fine mesh copper grid.
The carbon films were coated by a Edward 303 vacuum coating unit at a vacuum of 10^{-4} Torr. The powders were dispersed in methanol and agitated with ultrasound for 10 min. Two drops from the topmost layer of this suspension were dropped on the support film.

2.4.8. Dielectric measurements

At low frequencies, the determination of dielectric constant is usually based on the measurement of capacitance of a parallel plate capacitor or coaxial capacitor containing the material under test. The technique is based on the principle that when a material is introduced between the plates of a parallel plate capacitor, its capacitance increases by a factor \( \varepsilon' \), the dielectric constant of the material. The dielectric constant \( \varepsilon' \) is related with the capacitance \( C \) as

\[
\varepsilon' = \frac{Cd}{\varepsilon_0 A}
\]

Where \( \varepsilon_0 \) is the permittivity of free space (8.85x10^{-12} \ f/m), \( A \) is the cross sectional and \( d \) is the thickness of the specimen.

The dielectric properties of the viz. dielectric constant (\( \varepsilon' \)) and loss properties of the factor (tan \( \delta \)) of the materials have been studied using a complex impedance analyzer (Model Hewlett Packard, 4192) in the frequency range 30 Hz to 13 MHz both at room temperature and liquid nitrogen temperature. The materials used for the dielectric measurements were sintered to high density (>97%) in the form of circular discs of diameter \(~10\ \text{mm}\) and thickness \(~1\ \text{mm}\). The sintered specimens were mechanically polished and cleaned the surface with acetone. Room temperature curing silver paint was pasted on both the surfaces and was dried in an electric oven at a temperature of \(~100^\circ\text{C}\) for 4 h. Copper leads were taken from the silver electrode surfaces. This was used as the sample for
dielectric measurements. The capacitance and dissipation factors were directly measured from the impedance analyzer both at room temperature and liquid nitrogen temperature. For the measurements at liquid nitrogen temperature, the samples were well-immersed in liquid nitrogen taken in a thermostatic flask.

2.4.9. Resistance measurements

Resistance measurements are one of the important tools to characterize a superconductor sample. The superconducting transition temperature (Tc) can be directly determined by resistance measurements of the sample as a function of temperature. In the present study standard four-point probe method was used for the resistance measurements of the superconductor-insulator and superconducting thick film samples. The four-probe method of measuring the resistance has the advantage over two-probe method that the effects due to contact resistance, lead resistance etc can be avoided.

Four probe technique in van der Pauw geometry permits the measurement of an isotropic sample of uniform flat thickness but with arbitrary shape if meet the following criteria [14, 15]. The different criteria are, (i) the contacts are at the periphery of the sample, (ii) the contacts are sufficiently small, (iii) the sample is uniform in thickness, (iv) the sample does not contain holes, and (v) the sample is homogeneous. The measurement is based on a theorem, proved by van der Pauw [14, 15], for a sample of uniform thickness and for arbitrary shape with four arbitrarily positioned contacts (A,B,C&D) on the edges as shown in figure 2.3.
If we define

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

(9)

and

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

(10)

where \( V_D - V_C \) is the potential difference between contacts D and C caused by the passage of current I from A to B, etc. van der Pauw theorem takes the form

\[ \exp(-\pi R_{AB,CD} d / \rho) + \exp(-\pi R_{BC,DA} d / \rho) = 1 \]  

(11)

Where \( \rho \) is the resistivity and \( d \) is the sample thickness. This equation can be solved for \( \rho \), we get

\[ \rho = (\pi d / \ln2) \{ (R_{AB,CD} - R_{BC,DA}) / 2 \} \{ F(R_{AB,CD}) / (R_{BC,DA}) \} \]  

(12)

Here \( F \) is a function of the ratio resistance such that

\[ (R_{AB,CD} - R_{BC,DA}) / (R_{AB,CD} + R_{BC,DA}) = F \arccosh \{ \exp(\ln2 / F) \} / 2 \]  

(13)
In the special case of samples and constants which are in variant under rotation of 90°C, the sheet resistance $Rs = \rho / d$ reduces to simple form

$$Rs = \rho / \ln(2) \left( \frac{V}{I} \right) = \left( \frac{\pi}{\ln 2} \right) R_{AB,CD} = \left( \frac{\pi}{\ln 2} \right) R_{AC,BD}$$

(14)

Specimens with such symmetry are often easily prepared. Here $V$ is the voltage between two voltage contacts and $I$ is the current flowing through two current contacts.

The resistivity measurements can be made with either direct or alternating current. With direct current care must be taken to eliminate the effects of thermoelectric voltages in the voltage circuit by frequency reversing the sample current.

In the present study, the specimen is mounted on a copper block, which is attached to one end of a copper tube. The sample is electrically insulated from the copper block applying a thin layer of insulating varnish between the specimen and copper block. Four copper leads were attached symmetrically on the periphery of the sample using conducting silver paste. The schematic diagram of the resistance measurements is shown in figure 2.4. A calibrated copper constantan thermocouple was fixed to the copper block very close to the sample to measure the temperature of the sample. The sample holder set up was introduced in to a cylindrical vessel. The vessel was evaluated and a small amount of nitrogen gas was introduced. The whole set up was then introduced in to liquid nitrogen Dewar. Resistance measurements were made at close intervals while the sample was
continuously cooled at a low rate. The experiment was conducted by cooling the sample continuously and taking the readings at close intervals. The rate of cooling was controlled by introducing appropriate amount of nitrogen gas into the vessel as well as by raising the Dewar smoothly and slowly by means of a lab jack. A Keithley nanovoltmeter model 181 was used for resistance measurements. A Keithley electrometer model 602 was used for measuring higher values of resistance.
2.4.10 Current density measurements

The critical current density \((J_c)\) of the superconducting films was measured at 77 K in zero magnetic fields by direct method. Superconducting films were developed on a rectangular substrate of dimension 15 mm (length) and 2 mm (width) was used for current density measurements. Four contacts were given linearly as shown in Figure 2.5. In the present study, 1\(\mu\)V criterion was followed for the determination of \(J_c\). All other set for current density measurements were same as that employed for resistivity measurements except the current source and the linear contacts.

![Diagram of current density measurement](image)

**Figure 2.6:** Schematic diagram of current density measurement showing sample (S), storage cell (C), rheostate (R), ammeter (A), and nanovoltmeter (V)
REFERENCES


