CHAPTER 2
PREPARATION AND CHARACTERIZATION TECHNIQUES

2.1 Introduction

One of the major challenges in the development of advanced ceramic materials for various applications is the powder synthesis and their characterization. The processing of advanced ceramic materials involves the preparation of high purity single phase materials followed by densification which gives the final product. The properties and microstructure of the finished product depends on the technique used for powder preparation. The major problems faced during the preparation of ceramic powders are inhomogeneity, non-uniformity in terms of particle size and shape, impurity levels and lack of reproducibility of the final product. This chapter gives a brief description on various methods of preparation of ceramic materials and the different techniques used for their characterization. Specific details on the sample preparation and characterization are discussed in detail in the respective chapters.

2.2 Preparation of Ceramic Materials

The different powder preparation techniques used for the synthesis of advanced ceramic materials can broadly be classified into three major categories viz solid phase synthesis, liquid phase synthesis and gas phase synthesis. The solid phase synthesis or the solid state reaction method involves a series of mixing, grinding and heating cycles with varying heating schedules. Though being a widely accepted and conventional process, the solid-state reaction method has certain disadvantages. Agglomerates present in the calcined powder would result in high porosity and poor mechanical properties of the final product. Inadequate mixing of powders can lead to compositional inhomogeneities, insufficient stoichiometry control and formation of extraneous phases. Hence, it is necessary to optimize the type, purity and form of constituents and also the
medium of mixing. In the case of multicomponent systems, the mixing of the individual reactants is a very important factor as sufficient interaction of the powders is a necessity for a complete solid state reaction during the calcination process. The techniques involving the liquid and vapour phase synthesis have the advantage of obtaining greater homogeneity and reproducibility as compared to the conventional solid state synthesis. In the case of liquid phase synthesis, it is possible to obtain in solution, a better mixing of the constituents prior to high temperature processing. Moreover, powders of uniform morphology and microstructure can be obtained through solution based methods. Vapour phase methods have also gained attention in the preparation of advanced ceramic materials. One of the advantages is that fine particles of uniform size and distribution can be synthesized directly from the vapours in a very short duration. However, a very sharp monitoring is necessary to obtain powders of desired morphology and stoichiometry.

In the present study, the newly developed ceramic materials were prepared as micron sized particles by the conventional solid state reaction method and as nanosized particles by a modified combustion process. In order to synthesize the ceramic materials through the solid state reaction method stoichiometric amounts of oxides/carbonates/nitrates were weighed and thoroughly mixed in an agate mortar with acetone as the wetting medium. The mixture was then dried in an oven at about 150°C for ~ 2h. The dried mixture was calcined in air at an optimised temperature characteristic of each compound for 12 to 15 h in a alumina/platinum crucible. The resulting powder was ground well and the calcination step was repeated 2 to 3 times. The details of the calcination temperature, rate of heating, duration of heating etc., for each of the newly developed ceramic materials are described in detail in the respective chapters. Figure 2.1 gives the procedure followed in the present study for the preparation of ceramic materials by the solid state reaction method.
In order to synthesize nanoparticles of the newly developed ceramic materials, the required ions were obtained in solution by dissolving a stoichiometric mixture of the required carbonates and oxides heated at 1200°C for 4 h, in boiling nitric acid. Required amounts of citric acid and ammonia were added to the above solution. The solution was heated on a hot plate at 250°C. The solution boils and gets dehydrated followed by decomposition producing a foam. The foam then ignites to give a highly voluminous and fluffy product of combustion. The as prepared phase pure nanopowders were then sintered in air at a desired temperature for a specific duration. The details of the various steps involved in the preparation of these nanopowders are given in the respective
chapters. Figure 2.2 summarizes the steps followed in obtaining nanopowders of the ceramic materials by the modified combustion method.

![Diagram of the procedure for preparation of advanced ceramic materials by the modified combustion method.](image)

**Fig 2.2** Procedure for preparation of advanced ceramic materials by the modified combustion method

The phase pure ceramic powders were then heated at appropriate temperatures for specific durations (sintering) below the melting point of the compounds to obtain strong and dense products. In the course of sintering, surface area decreases and consequently the free energy excess associated
decreases which results in the shrinkage. In the initial stages of sintering, adhesion of the loosely attached grains take place and during the final stages, elimination of the pores take place due to mass transport from the intergrain contacts towards the pores. In the present study, the single phase powders were shaped as circular discs of dimensions 11 mm diameter and ~ 1.5 mm thickness under a uniaxial pressure of 250 MPa. These circular discs were then sintered in air at an optimised temperature for a specific duration, details of which are given in the following chapters.

2.3 Preparation of Thick Films

Thick films of high temperature superconducting (HTSC) materials can be fabricated by screen printing, spin coating, spray pyrolysis, paint on method, dip coating etc. In the present study, thick films of high temperature superconductors have been prepared by the dip-coating technique followed by melt texturing. Dip coating is a relatively simpler technique and can be used to prepare films of very small thickness (2 – 5 μm). An added advantage of the dip coating technique is that coating surfaces which are not plane can be used and both the surfaces of the substrate can be coated, if necessary. In the dip-coating technique a suspension of the high temperature superconducting material is prepared by thoroughly mixing fine HTSC powder with isopropyl alcohol or n-butanol. The viscosity of the suspension is controlled by adding commercially available fish oil. The polished and cleaned well sintered substrate is dipped in the thick film suspension and the dipping process is repeated till the required thickness is obtained for the film. The resulting film is then dried in a hot air oven and processed in a programmable furnace following specific heating schedules, the details of which are described in the respective chapters.

2.4 Characterization Techniques

The various techniques used in the present study for the characterization of the newly developed ceramic powders are powder x-ray
diffraction technique, differential thermal analysis, thermogravimetric analysis, surface area analysis, particle size analysis, infrared spectroscopy and high resolution transmission electron microscopy. The dielectric properties of the sintered samples were studied by using a complex impedance analyser. The superconductivity studies were carried out by the temperature resistivity and critical current density measurements using the standard four probe technique. The microstructural studies of the sintered ceramic samples were carried out using the scanning electron microscopy.

2.4.1 X-ray Diffraction Technique

X-ray diffraction is one of the most important and powerful tools for the determination of crystal structures and phase analyses of ceramic materials. Characteristic x-ray diffraction patterns are produced when the wavelength of the electromagnetic radiation interacting with the specimen is comparable to that of the interatomic spacing in crystals. X-rays have wavelengths comparable with the interatomic spacing in crystals. When x-rays of wavelength comparable or smaller than the lattice constants are allowed to fall on a crystal, one or more diffracted beams are observed in directions quite different from that of the incident beam. W. L. Bragg explained the observed angles of the 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 a very small fraction of the radiation. Diffracted beams are found only when the reflections from parallel planes of atoms interfere constructively.

Bragg showed that when an x-ray radiation is incident on a series of parallel $(hkl)$ planes spaced at equal distances $d_{hkl}$ apart, and when the path difference for the x-rays reflected from adjacent planes, $2d_{hkl} \sin \theta$ (where $\theta$ is the angle which the incident beam makes with the plane of the crystal) is an integral multiple of the wavelength $\lambda$, constructive interference of the radiation reflected from the successive planes occurs. Thus, the condition for constructive
interference of the reflected radiation is given by \(2d_{hkl} \sin \theta = n\lambda\). It is observed that, although the reflections from each plane is assumed to be specular, only for certain values of \(\theta\) will the reflections from all parallel planes add up in phase to give a strong reflected (diffracted) beam. The Bragg’s law is a consequence of the periodicity of the space lattice. Bragg reflections can occur for wavelengths \(\lambda < 2d_{hkl}\) (1).

![Schematic diagram of a Powder X-ray Diffractometer](image)

*Fig. 2.3 Schematic diagram of a Powder X-ray Diffractometer*

In the present study, powder method is employed for the identification of the crystalline phases present in the ceramic sample. The XRD pattern is a unique characteristic property of a material resulting from the arrangement of atoms. Each material has a unique crystal structure which in turn produces characteristic XRD patterns. Identification of the phases is done by comparing the \(d\) spacing and \((I/I_0)\) of the observed XRD pattern of the sample with standard
reference data. In the present study, the samples for XRD studies were prepared by smearing the powder of the ceramic material on a flat glass sample holder provided with a groove for holding the powder. A computerised Rigaku X-ray diffractometer (model D_{max}/2C, Japan) with Ni filtered CuKα radiation (λ = 1.5406Å) was used for the characterization of the samples.

2.4.2 Differential Thermal Analysis

Differential thermal analysis (DTA) is a thermal technique used to detect the physical and chemical changes taking place in a material when its temperature is increased or decreased at a uniform rate. It is a qualitative study especially suited for studying the structural change within a material at elevated temperatures. In this technique, the temperature of the sample is compared with the temperature of a thermally inert material and is recorded as a function of the temperature (2).

![Fig. 2.4 Schematic diagram of a Differential Thermal Analyser (DTA)]

In DTA, highly sensitive thermocouples detect the temperature difference (ΔT) between the sample and the inert reference (fig. 2.4). In the present study, differential thermal analysis was carried out using a Shimadzu DTA – 50A
unit (Japan) with alpha alumina as the reference material which does not undergo any enthalpy change till its melting point. The samples were heated in nitrogen atmosphere at a heating rate of 10° C/min from room temperature to 1300° C.

2.4.3 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is also a thermal technique (3) used to determine changes in sample weight, which may result from chemical or physical transformations, as a function of temperature or time. This technique measures and automatically records changes in weight as a function of temperature and the data provides information regarding the thermal stability, composition and decomposition behaviour (fig. 2.5). The results obtained from the thermogravimetric analysis is often used in conjunction with the differential thermal analysis results to obtain a good quantitative estimation of the solid state reaction. These two techniques are complementary to one another. In the present study, thermogravimetric analysis was carried out using a Shimadzu TGA – 50 (Japan) unit. The samples were heated at a heating rate of 10° C/min in nitrogen atmosphere from room temperature to 1100° C.

![Fig. 2.5 Schematic diagram of a Thermogravimetric Analyzer](image-url)
2.4.4 IR Spectroscopy

The presence of any organic residues in a material is detected with the help of the infrared spectroscopy. The principle in this technique lies in the fact that when an infrared radiation interacts with the material, the various chemical bonds present in the material absorb the radiation and vibrate accordingly (4). In the present study, the FT-IR spectrum was recorded using a Nicolet 1 400D FT-IR spectrometer (fig. 2.6). The material to be examined was finely dispersed in KBr and pressed in the form circular disc of dimensions 10 mm diameter and \(~0.5\) mm thickness under a pressure of 250 MPa. These pellets were then dried and the FTIR spectrum was recorded from 400 to 4000 cm\(^{-1}\).

![Fig. 2.6 Schematic diagram of a FT-IR Spectrometer](image)

2.4.5 Agglomerate Size Distribution

The agglomerate size distribution studies were carried out using the sedimentation technique, which is based on the fact that the rate of fall of a particle in a fluid medium is proportional to the volume of the particle. The rate of fall \((v)\) of a spherical particle is related to the diameter \((d)\) of the particle by
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.

In the present study, the agglomerate size distribution of the nanosized powders were studied by using a Micromeritics sedigraph model 5100. The powders were ultrasonically dispersed in water before the agglomerate distribution curve was recorded.

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

2.4.6 BET Surface Area Measurement

Surface characteristics study of fine powders is one of the most popular, at the same time difficult technique in ceramic characterization. All surface characteristics are a consequence of asymmetrical or unbalanced forces between atoms and molecules at the interface of a particle and are electronic in origin. The widely used technique to determine the specific surface area of fine powders is the BET (Brunauer, Emmett and Teller) model (5). The amount of nitrogen gas absorbed by a powder sample at liquid nitrogen temperature over a range of gas partial pressures is measured in the BET model (fig. 2.7).

![Schematic diagram of a Gas Adsorption Apparatus based on the BET model](image)

Fig. 2.7 Schematic diagram of a Gas Adsorption Apparatus based on the BET model
The amount of gas forming a monolayer of the powder surface is calculated using the equation

\[
\frac{P}{V(P_o - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \cdot \frac{P}{P_o}
\]

where

- \(V\) = total volume of gas adsorbed
- \(V_m\) = gas adsorbed when the adsorbent surface is covered with a unimolecular layer
- \(P\) = equilibrium pressure of the system
- \(P_o\) = saturation pressure of the adsorbate gas
- \(C\) = a constant dependent on the heat of absorption and heat of liquefaction of the adsorbate

The specific area of the gas powder is obtained from the relationship

\[
S = \frac{V_m \sigma N}{V_i W}
\]

where

- \(\sigma\) = area occupied by one molecule of adsorbate
- \(N\) = Avagadros’ number
- \(W\) = weight of the powder sample
- \(V_i\) = ideal gas volume

The average particle size of the powder was calculated from surface area values by assuming that they all consisted of monosized hard spherical particles. The particle size is given by (6),

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

where \(\rho\) is the density of material and \(S\) is the surface area.
2.4.7 Scanning Electron Microscopy

The properties of ceramic materials are closely related with its microstructure. Therefore, the analysis of the microstructure of ceramic materials can give detailed information regarding grain morphology and size, presence of additional phases, surface defects, cracks, pores etc. In the present study the microstructural analysis of the sintered samples were carried out using a JEOL JSM - 5600 LV (Japan) scanning electron microscope (SEM).

The SEM employs electromagnetic lenses, vacuum systems, apertures and electron guns. A schematic diagram illustrating the basic parts of the SEM is given in fig.2.8. In an SEM, the electrons emitted by a heated filament is accelerated and then collimated into a narrow beam. It is then allowed to fall upon the specimen surface, producing several different imaging possibilities. Because of the aperture size and short wavelength of electrons, tremendous depth of field can be realised.

*A narrow beam of electrons from the electron gun is focussed by electromagnetic lens into a small spot (less than 10 nm) on the surface of the*
specimen. Deflector coils then scan the beam across the specimen. In the most common imaging mode, secondary electron imaging (SEI), the high energy primary beam dislodges electrons from the atoms near the surface of the specimen (secondary electrons), some of which then strike the SEI collector. Electrons which strike the collector produce photons that are then processed by a photoamplifier circuit connected to the cathode ray tube (CRT). An electron that interacts with the collector results in a voltage applied to the gun of the CRT, which produces a point of illumination on the CRT screen. The scan generator that operates the scanning coils controlling the electron beam within the SEM column is connected to the deflector plates of the CRT. Thus, as the SEM beam is scanned over the specimen, the CRT gun is simultaneously scanned over the CRT screen. The output of the photoamplifier (voltage) is employed to modulate the brightness of the CRT beam in synchronization with the SEM electron beam. The current of secondary electrons recorded by the collector at a given point in time produces a given voltage after processing by the photomultiplier circuit, determining the brightness of the spot of the CRT. Any variation in the elemental composition, texture or topography can result in a variation in the current reaching the collector. The specimen magnification is determined by the relationship between the distance scanned on the specimen surface by the primary beam and the distance scanned on the CRT during the same period (7).

The use of an electron gun needs a vacuum system and the type of the gun used determines the type of the vacuum system needed. Most of the SEMs have accelerating voltages adjustable from 0-35 kV and have three electromagnetic lenses, the first two of which defocus the beam, the third being used to determine the final diameter of the beam striking the specimen surface. Working distance can be varied by placing the specimen higher or lower in the column, which also places the specimen nearer to or further away from the electron source and collector respectively. Moving the specimen further away from the lens and collector increases the depth of field and can reduce charging
to some extent. The insulator samples for SEM analysis are coated with gold in order to improve the surface conductivity which prevents the accumulation of negative surface charge which might interact with the secondary electrons. The coating of non-conducting specimens improves the signal. For the SEM analysis of conducting specimens no coating is required.

2.4.8 Transmission Electron Microscopy

Transmission electron microscopy is a 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

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

Where V is the accelerating voltage

The resolving power of any optical instrument which is limited by diffraction, is proportional to the wavelength of the radiation used to illuminate the specimen. In the case of good microscope that uses visible light, maximum useful magnification is about 500 x, higher magnification gives larger images but do not reveal any more detail. 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. The block diagram of a transmission electron microscope is as shown in fig.2.9.

In transmission electron microscopy, electrons of higher energy are allowed to transmit, through the replica (about 200 Å thick) of the specimen surface. Some electrons will be transmitted and the replica will diffract some of them as the electron beam strikes. If the transmitted electron beam is used for the generation of micrographs, such pictures are called bright field micrographs. In the 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 elucidation of crystal structure (8).

Fig. 2.9 Block diagram of Transmission Electron Microscope
In the present study, the morphology and structure of the materials were studied by a JEOL 2000 EX II high resolution transmission electron microscope (HRTEM) operated at 200 kV 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 an ultrasound for 10 minutes. Two drops from the topmost layer of this suspension were dropped on the support film.

2.4.9 Dielectric Measurements

The dielectric properties of the newly developed sintered ceramic compounds have been studied using a complex impedance analyser (Hewlett Packard Model 4192 A, USA) in the frequency range 30 Hz to 13 MHz. The samples for dielectric measurements were prepared in the form of compact circular discs with dimensions 10 mm diameter and ~ 0.5 to 1.0 mm thickness. Both the faces of the samples were polished and cleaned well in running water. A very thin and uniform coating of silver paste was applied on both the faces of the polished samples and copper leads of suitable length were fixed on both the faces of the disc using silver paste. The circular discs were then dried in an oven at a temperature of ~100°C. The capacitance (C) and the dissipation factor (tan δ) were directly measured from the impedance analyser and the measurement was carried out by varying the frequency. The dielectric constant (ε') of the samples were calculated by substituting the values of capacitance in the formula $C = \frac{\varepsilon_0 \varepsilon'A}{d}$, where $\varepsilon_0$ is the permittivity of free space ($\varepsilon_0 = 8.854 \times 10^{-12} \text{ Fm}^{-1}$), d, the thickness of the sample and A, the area of cross section of the sintered specimen.

2.4.10 Resistivity Measurements

Resistivity measurement is one of the important techniques used to characterize a superconducting sample as a function of temperature. In the
present study, the standard four probe technique was made use for the resistivity measurements of the superconducting samples and the thick films. 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. Moreover, a set of readings can be taken for a single sample by changing the applied current.

Four probe method of measurement in van der Pauw geometry permits the measurement of the resistivity of an isotropic sample of uniform flat thickness but with arbitrary shape if it meets the following criteria (14,15) : the contacts are at the periphery of the sample, the contacts are sufficiently smaller, the sample is uniform in thickness, the sample does not contain holes and the sample is homogeneous. The measurement relies on a theorem proved for a sample of arbitrary shape with leads as shown in Fig 2.10.

![Lead arrangement for van der Pauw with four contacts M,N,O and P on the periphery for resistivity measurements](image)

Fig. 2.10 Lead arrangement for van der Pauw with four contacts M,N,O and P on the periphery for resistivity measurements (ref.15)

The resistance $R_{MN}$ is defined as the potential difference $V_p - V_o$ between the contacts O and P when unit current is put through the contacts M and N.

\[
R_{MN, OP} = \frac{(V_p - V_o)}{I_{MN}}\]

2.6
Analogously,

\[ R_{NO, PM} = (V_M - V_P) / I_{NO} \]  \hspace{1cm} (2.7)

The new method of measurement is based on the theorem that between \( R_{MN, OP} \) and \( R_{NO, PM} \), there exists the simple relation,

\[ \exp (-\pi d R_{MN, OP} / \rho) + \exp (-\pi d R_{NO, PM} / \rho) = 1 \] \hspace{1cm} (2.8)

where \( d \) is the thickness of the lamella and \( \rho \) is the resistivity of the material. If \( d \) and the resistances \( R_{MN, OP} \) and \( R_{NO, PM} \) are known, then the equation 2.8 yields an equation in which \( \rho \) is the only unknown quantity. The solution is particularly straightforward if the sample possesses a line of symmetry. In that case M and O are placed on the line of symmetry while N and P are disposed symmetrically with respect to this line. Then,

\[ R_{MN, OP} = R_{NO, PM} \] \hspace{1cm} (2.9)

\( \rho \) can then easily be found from equation 2.9

\[ \rho = (\pi d / \ln 2) R_{MN, OP} \] \hspace{1cm} (2.10)

In general, it is not possible to express \( \rho \) explicitly in known functions. The solution can however be written in the form

\[ \rho = (\pi d / \ln 2) \{ (R_{MN, OP} + R_{NO, PM})/2 \} f \] \hspace{1cm} (2.11)

where \( f \) is a function of the ratio of resistance such that

\[ (R_{MN, OP} - R_{NO, PM})/(R_{MN, OP} + R_{NO, PM}) = f \arccosh \{\exp (\ln 2/f)/2\} \] \hspace{1cm} (2.12)

van der Pauw has given a graphical representation for \( f \) (fig.2.11). Thus to determine \( \rho \), we first calculate \( (R_{MN, OP} / R_{NO, PM}) \), taking the corresponding value of \( f \) from fig.2.11 and then finding \( \rho \) from equation 2.11.
In the spherical case of samples and contacts which are invariant under rotation of 90°, the sheet resistance $R_S = \rho/d$ reduces to the form

$$R_S = \frac{\pi}{1n2} \frac{V}{I}$$

$$= \frac{\pi}{1n2} R_{MN, OP} = \frac{\pi}{1n2} R_{NO, PM}$$ \hspace{1cm} 2.13

Specimens with such symmetry are often easily prepared. Here $V$ is the voltage between voltage contacts and $I$ is the current flowing between two current contacts. This equation has been extended by Versnel (11) to include the case of finite length contacts on structures which are invariant under 90° rotation.

In the present study, the sample whose resistivity is to be measured was mounted using a thin layer of insulating varnish on a copper block attached at the end of a copper tube. Four copper leads were attached on the periphery of the sample using conducting silver paste. A calibrated copper constantan thermocouple attached to the copper block very close to the sample was used for the temperature measurements. The whole setup was enclosed in a cylindrical vessel (Fig. 2.12). The vessel was evacuated and a small amount of nitrogen gas was introduced. The whole set up was then introduced into the liquid nitrogen dewar. The resistivity measurement with respect to temperature was conducted by cooling the sample at a slow rate and taking the readings at close intervals.
The temperature of the specimen was varied by raising or lowering the cylindrical vessel. To measure the resistance, a known current was passed through the current leads (usually 1 to 10 mA) and the voltage drop across the voltage leads was measured. A Keithley current source (model 220) was used for the above purpose. In the present study, the resistivity of the samples were studied in the temperature range 300 to 77 K. The thickness of the bulk samples were measured using a screw gauge.

![Schematic diagram of resistivity measurement setup](image)

**Fig.2.12 Schematic diagram of resistivity measurement setup**

### 2.4.11 Current Density Measurements

The critical current density \( (J_c) \) of the superconducting films were measured at 77 K in zero magnetic field. Superconducting films developed on a rectangular substrate of dimensions 10 mm x 2 mm were used for the current density measurements. Four contacts were given linearly as shown in figure 2.13.
Fig. 2.13 Schematic diagram of current density measurement showing sample (S), storage cell (C), rheostat (R), ammeter (A) and nanovoltmeter (V).

In the present study, 1μV/cm criterion was followed for the determination of the critical current density. All the other setup was similar as that used for the resistivity measurements except the current source and the linear contacts.
REFERENCES


Further References


