

EXPERIMENTAL

2.1 INTRODUCTION

This chapter reports the details of the experimental procedure for the synthesis of Yttrium copper titanate ceramic and its isomorphs along with different physiochemical techniques used for their characterization. Materials research in the area of electronic ceramics involves (i) Synthesis of various compositions in the system of interest, (ii) Single-phase analysis of the systems, (iii) Heat treatment at high temperature and (iv) Microstructural analysis (v) electric and dielectric behavior of the synthesized ceramics. In the present investigation, various samples in the systems (A) $Y_{2/3}Cu_3Ti_4O_{12}$ (YCTO) (B) $Y_{1/3}La_{1/3}Cu_3Ti_4O_{12}$ (YLCTO) (C) $Y_{2/3}Cu_{3-x}Zn_xTi_4O_{12}$ (YCZTO) ($x = 0.10, 0.20$ and 0.30) and (D) $Y_{2/3}Cu_3Ti_{4-x}Fe_xO_{12}$ (YCTFO) ($x = 0.05, 0.10, 0.15$ and 0.20) were synthesized by the semi-wet route. All the synthesized samples were characterized for their crystal structure, microstructure, electrical and dielectric characteristics.

2.2 MATERIALS USED

For the synthesis of required compositions in the above systems, we have used high purity chemicals viz, Yttrium nitrate, lanthanum oxide, bismuth nitrate, copper nitrate, Ferric nitrate, Zinc acetate, titanium dioxide and glycine with specifications given in Table 2.1.

Table 2.1: Specification of the materials used

Raw Materials	Minimum Assay	Manufacturer
Y(NO ₃) ₃ .6H ₂ O	99 %	HiMedia (India)
La ₂ O ₃	99 %	CDH, (India)
Bi(NO ₃) ₃ .5H ₂ O	98 %	Merk (India)
Cu(NO ₃) ₂ .3H ₂ O	99.5%	Merk (India)
Fe(NO ₃) ₃ .9H ₂ O	99.8%	Merk (India)
Zn(NO ₃) ₂ .6H ₂ O	99%	Merck (India)
TiO ₂	99 .5%	Merk (India)
Glycine	99.5%	Merk (India)

2.3 PREPARATION OF VARIOUS RAW MATERIALS

For the synthesis of compositions of undoped and doped YCTO ceramics by semi-wet route, the following solutions were prepared and their concentrations were estimated by the appropriate complexometric chemical methods described below:

2.3.1 Preparation of Ethylenediaminetetraacetic Acid (EDTA) Solution

The disodium salt of EDTA (Ethylenediaminetetraacetic acid) was dried for 12 hours at 80°C and cooled in a desiccated atmosphere so that the compound attained the composition of its dihydrate, Na₂C₁₀H₁₄O₈N₂·2H₂O (molar Mass = 372.24). One litre of 0.1M EDTA solution contained 37.224 g of this dried substance.

2.3.2 Preparation of Buffer Solution of pH 10

70.0 g of ammonium chloride were mixed with 570 ml of liquor ammonia (specific gravity 0.9), and the volume was made up to a litre using double distilled water.

2.3.3 Preparation of Eriochrome Black T Indicator

About 0.2 g of Eriochrome Black T (IUPAC name: sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate) was dissolved in a mixture containing about 15 ml of triethanolamine and about 5 ml of absolute alcohol.

2.3.4 Preparation of Metal Nitrate Solutions

- (a) **Ca:** An approximately 0.1 M solution of calcium nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Molar mass = 236.15), was prepared by dissolving about 23.615 g of the salt in one litre of double distilled water.
- (b) **Cu:** An approximately 0.1 M solution of copper nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Molar mass = 241.60), was by dissolving about 24.160 g of the salt in one litre of double distilled water.
- (c) **Fe:** An approximately 0.1 M solution of ferric nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Molar mass = 403.999), was prepared by dissolving about 40.399 g of the salt in one litre of double distilled water.
- (d) **Zn:** An approximately 0.1 M solution of zinc nitrate, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Molar mass = 297.49), was prepared by dissolving about 29.749 g of the salt in one litre of double distilled water.
- (e) **La:** An approximately 0.1 M solution of lanthanum nitrate, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Molar mass = 433.01185), was prepared by dissolving about 43.3012 g of the salt in one litre of double distilled water.

2.4 ESTIMATION VARIOUS RAW MATERIALS

2.4.1 Estimation of calcium ions in calcium nitrate solution

A known quantity of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was dissolved in distilled water to get its clear solutions. 25.0 ml of the calcium ion solution was taken in a 250 ml conical flask, diluted it with about 25 ml of distilled water and then added 2 ml of the buffer solution and two drops of the Eriochrome black T indicator. The resulting solution was titrated with standard 0.1M EDTA solution until the colour changes from wine red to blue. The titration was repeated to get three concordant readings which give the

volume of EDTA used. From this value, Ca^{2+} was estimated in the stock solution of Calcium nitrate.

2.4.2 Estimation of copper ions in copper nitrate solution

To a 50.0 ml of the copper salt stock solution was taken in a 250 ml conical flask and 10 ml. of potassium iodide solution was added. The solution turned dark brown. Initially, the solution was titrated with the thiosulphate solution with constant stirring. When the colour of the liquid became pale yellow, it was diluted to 200 ml with double distilled water and 2 ml of starch solution was added as an indicator. The titration was continued with the resulting blue solution until the colour changed from blue to colourless.

2.4.3 Estimation of ferric ions in ferric nitrate solution

To 10 ml of iron nitrate stock solution, a pinch of zinc-dust and 5 ml conc. H_2SO_4 was added. The solution was left as such for some time till zinc dissolves, reaction is completed and no more bubbles of hydrogen gas appeared. In this process, all ferric ions got converted into ferrous ion. To this solution, 3-4 drops of N-Phenylanthranilic acid (indicator) were added and the solution was titrated against standard of $\text{K}_2\text{Cr}_2\text{O}_7$ solution to get total iron content.

2.4.4 Estimation of magnesium ions in magnesium nitrate solution

10.0 ml of the magnesium ion solution was taken in a 150 ml conical flask and diluted it with about 25 ml of distilled water and added 15 ml of the buffer solution of pH 10 and added few drops of Eriochrome black T indicator to produce a light wine-red color. The solution was titrated with standard 0.1M EDTA solution until the colour changed from wine red to blue. This colour change marked the endpoint.

2.4.5 Estimation of zinc ions in zinc nitrate solution

The reaction of Zn^{2+} with EDTA may be expressed as:



This reaction can be used to determine the concentration of zinc ion by using an EDTA standard solution and an indicator which can form a colored complex with Zn^{2+} . 25ml of Zn^{2+} solution was pipetted into a 250 ml conical flask and then it was

diluted with distilled water to approximately 100 ml. 10ml of the buffer solution and 2-3 drop of the indicator was added to it and was titrated slowly and carefully with standard EDTA solution until at the end point colour changes from wine red colour to blue. After getting a concordant reading, the concentration of Zn^{2+} in g/ml was calculated.

2.5 SYNTHESIS OF MATERIALS

2.5.1 Synthesis of Materials by Semi-wet Route

The Semi-wet route is modified sol-gel technique. It is also called as citrate-nitrate gel chemical method, a type of combustion synthesis technique. Combustion synthesis is used to obtain multi-component single phase material. The combustion method is based on the redox reaction between a fuel and oxidant present in the precursor solution. Glycine or citric acid was used as a fuel while nitrates of different metals are used as an oxidant. Some chelating agents like EDTA, acetic acid, etc. can form complex with metal ions present in the precursor solution and act as fuel. This complex, on dehydration, produces a viscous gel which on further heating self-ignites with the evolution of huge amount of gases. It leads to the development of porous floppy ash. Single phase powder can be obtained by further calcination of the ash at high temperature.

In this route, 0.1 molar standard solutions of nitrates of each of Yttrium (Y), copper (Cu), zinc (Zn) and iron (Fe) were prepared using distilled water. Solutions of metal nitrates in stoichiometric amounts were mixed in a beaker. Stoichiometric amounts of solid TiO_2 and aqueous solution of glycine (equivalent to each metal ion) were added to the solution. The solution was heated on a hot plate with a magnetic stirrer at 70-80 °C to evaporate water. Dehydration of the homogeneously mixed solution during heating caused the development of a gel. This gel on further heating self-ignites followed by its swelling. This ignition product ash was voluminous and floppy in nature. This ash was calcined in air at 800 °C for 8h in a muffle furnace. The resultant mixtures were ground into fine powder using a pestle and mortar. Few drops of 2% PVA were used as a binder. The cylindrical pellets were made using a hydraulic press and were sintered at 950 °C for 12h for dielectric measurements.

A flow chart showing the various steps in the preparation of these materials by this method is shown in the Fig. 2.1.

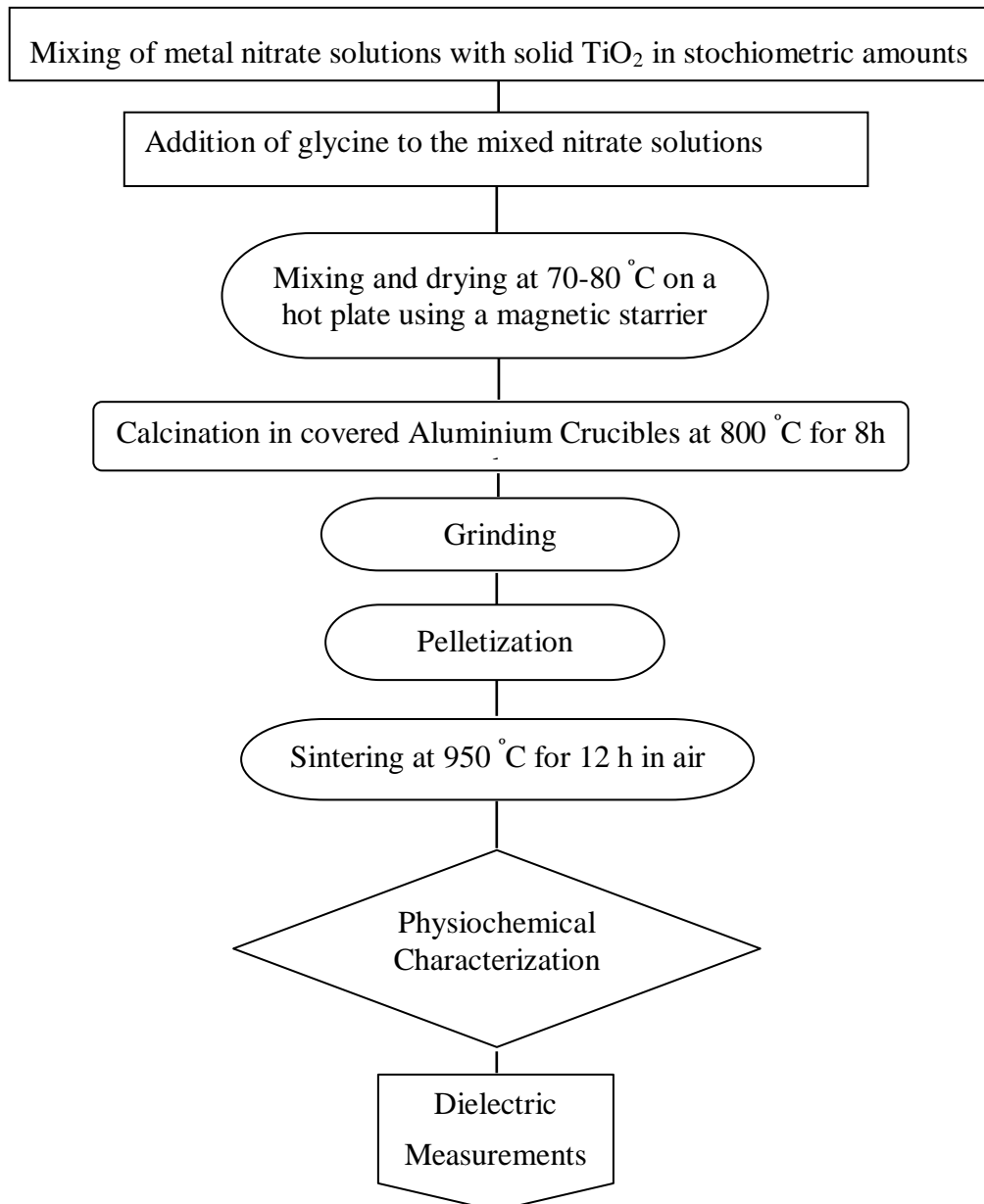


Figure 2.1: Flow chart for the synthesis of materials by the semi-wet route

2.5.2 Calcination Process

Calcination is a heat treatment process applied to solid materials to bring about a thermal decomposition, phase transition, or removal of a volatile fraction. The heating is operated below the melting point of the product materials. The blue gel obtained during experiment was calcined in air at 500 °C for 5 hrs and further 800 °C for 8 hrs in a Muffle furnace.

A schematic diagram of processing and analysis of dry ceramic powder is shown in the following Fig. 2.2.

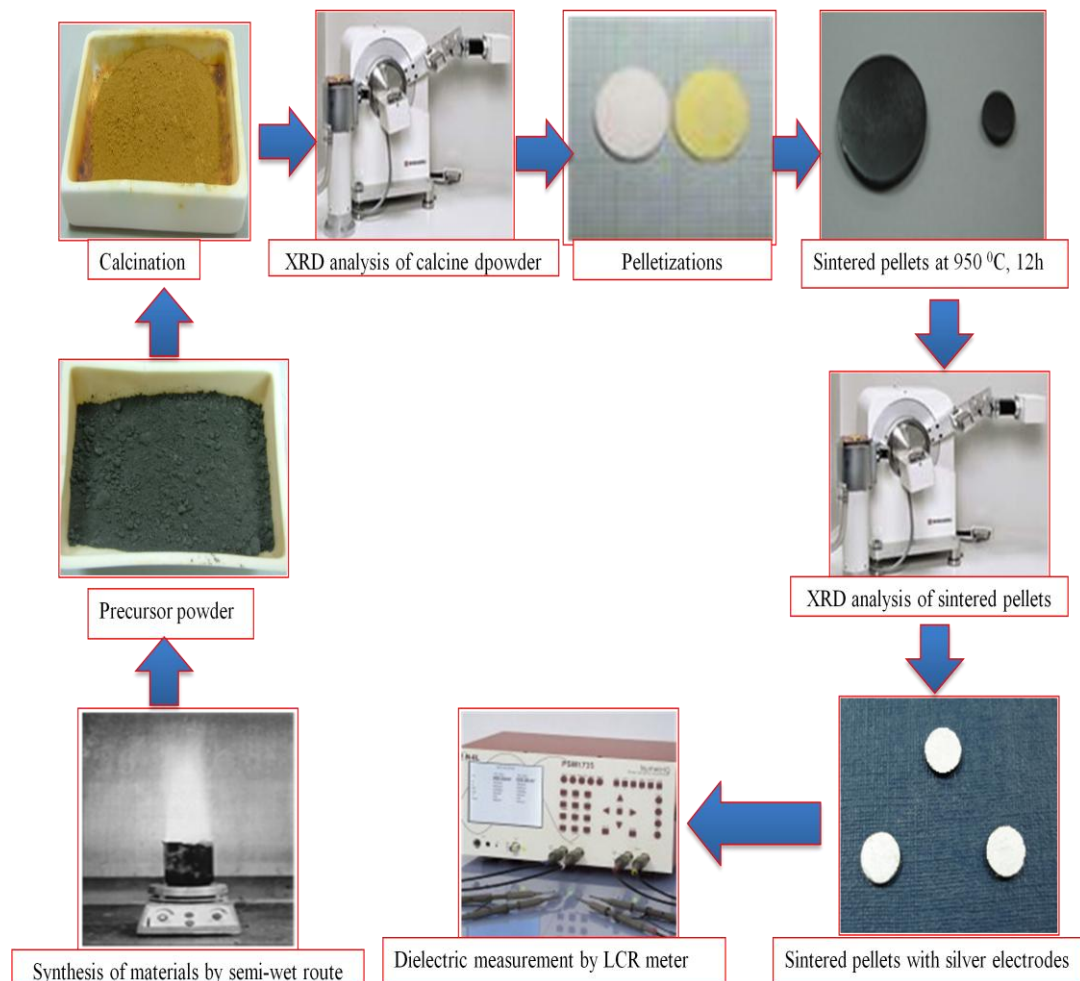


Figure 2.2: Schematic steps of processing and analysis of electro-ceramic.

2.5.3 Pressing and Sintering of Samples

The calcined powder was transferred to an agate mortar and ground into fine powder. A few drops of 2% polyvinyl alcohol were added and mixed well with the powder. Powders were pressed into cylindrical pellets (10 mm × 1 mm) with the help

of a hydraulic press by applying pressure 4-5 tons. These pellets were kept in a ceramic crucible, covered with a lid and heated slowly to 500 °C and kept at this temperature for about two hours to burn off the binder completely.

Sintering is a process of densification of a porous compact by heating it to an appropriate temperature. These pellets were maintained at their respective sintering temperatures for a suitable period. Thereafter, the temperature was raised to the required sintering temperature at which both sintering as well as solid-state reaction amongst various constituents took place. These pellets were maintained at 950 °C temperatures for 12 h.

The calcination and sintering temperature applied for different compositions are also given in the Table 2.2.

Table 2.2: List of single-phase compositions prepared in various systems and their firing schedules

S. No.	System	Composition	Code	Calcination		Annealing	
				Temp. (°C)	Time (h)	Temp. (°C)	Time (h)
1.	$Y_{2/3}Cu_3Ti_4O_{12}$	---	YCTO	800	8	950	12
2.	$Y_{1/3}La_{1/3}Cu_3Ti_4O_{12}$	---	YLCTO	800	8	950	12
3.	$Y_{2/3}Cu_{3-x}Zn_xTi_4O_{12}$	$Y_{2/3}Cu_{2.90}Zn_{0.10}Ti_4O_{12}$	YCZTO 1	800	8	950	12
		$Y_{2/3}Cu_{2.80}Zn_{0.20}Ti_4O_{12}$	YCZTO 2	800	8	950	12
		$Y_{2/3}Cu_{2.70}Zn_{0.30}Ti_4O_{12}$	YCZTO 3	800	8	950	12
4.	$Y_{2/3}Cu_3Ti_{4-x}Fe_xO_{12}$	$Y_{2/3}Cu_3Ti_{3.95}Fe_{0.05}O_{12}$	YCTFO 1	800	8	950	12
		$Y_{2/3}Cu_3Ti_{3.90}Fe_{0.10}O_{12}$	YCTFO 2	800	8	950	12
		$Y_{2/3}Cu_3Ti_{3.85}Fe_{0.15}O_{12}$	YCTFO 3	800	8	950	12
		$Y_{2/3}Cu_3Ti_{3.80}Fe_{0.20}O_{12}$	YCTFO 4	800	8	950	12

2.6 CHARACTERIZATION OF MATERIALS

2.6.1 Thermal Analysis:

The thermogravimetric (TG) and differential thermal analysis (DTA) are the techniques which measure a change in a material as a function of temperature. It is useful in characterizing decomposition and crystallization during ceramic powder processing and in determining an optimum calcination temperature. In TG/DTA techniques a precursor powder specimen and an inert reference material are heated concurrently at a linear rate each having its temperature sensing and recording apparatus. The thermal energy changes, either endothermic or exothermic which occur in the course of heating are plotted. These plots provide data on the chemical and physical transformations such as melting, sublimation, glass transitions, crystal transitions and crystallization. A thermogravimetric analyzer (Pyris Diamond TG/DTA, Perkin-Elmer Instrument, USA) is used to characterize the material mass change either as a function of temperature or isothermally as a function of time in a controlled atmosphere. It can be used to characterize a material that exhibits a weight change due to decomposition, oxidation or dehydration. In this analysis about 20 mg dry precursor powder of materials were placed in the sample holder and then heated from room temperature to 1000 °C with heating rate of 10 °C/minute in nitrogen atmosphere. TG curve shows the variation of mass of the material as a function of temperature. In DTA, the samples under study and an inert reference are made to undergo identical thermal cycles while recording any temperature difference between sample and reference. This differential temperature is then plotted against time or against temperature to get DTA curve or thermogram. The change in the sample, either exothermic or endothermic, can be detected about the inert reference. Through this analysis, energy required for a particular type of phase transformation in the material can be determined. DTA curve provides data on the transformations that have occurred, such as phase transitions, crystallization, melting and sublimation.

2.6.2 X-Ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) is a powerful technique used primarily for crystallographic characterization of solid materials. It is one of the primary method used by material scientist and solid state chemists to examine the physicochemical

make-up of unknown solids. XRD analysis provides structural information of bulk materials and thin film and also the composition of crystallographic phases present in a sample. It is based on the fundamental principles that the angle of reflection of X-rays from a sample is related to the crystal structure and composition of the material. XRD can provide structural information of bulk materials and thin film, and also the formation of crystallographic phases present in a sample.

X-ray diffraction spectra of sintered powders of ceramics were recorded using X-ray diffractometer (MiniFlex2 Goniometer. Rigaku, Tokyo, Japan) under 30kV/15mA -X-Ray, $2\theta/\theta$ –continuous scanning mode within the scanning range $20-90^\circ$) instrument employing Cu- K_α radiation ($\lambda=1.54059 \text{ \AA}$) using Ni-filter. The sample was scanned at rate of $4^\circ/\text{minute}$. XRD data were indexed by comparing with standard data reported earlier on the parent compound. The formation of single phase of the material was confirmed by the absence of characteristic lines of constituent oxides in the powder XRD patterns. Lattice parameters and lattice volume were determined by least square fitting of XRD data using a software program ‘CEL’.

2.6.3 Density and Porosity Measurements

The density of the sintered pellets was determined from the geometrical dimensions and their mass as well as using Archimedes principle. Theoretical density was determined from the molecular weight of the compound, and lattice parameters. The total porosity, in percentage, was calculated using the relation

$$\% \text{ porosity} = [(D_{\text{theo.}} - D_{\text{exp.}}) / D_{\text{th.}}] \times 100 \quad (2.1)$$

where $D_{\text{theo.}}$ and $D_{\text{exp.}}$ represent theoretical density and experimental density respectively.

2.6.4 Scanning Electron Microscopy (SEM) Analysis

The Scanning Electron Microscopy is widely used to examine microscopic structure by scanning the surface of materials. It uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. SEM was used to study the dispersion uniformity of the filler particles, the size of the agglomerate, and the

connectivity between filler particles. For SEM analysis, the cross section of a sample was polished before observation. In the case of non-conductive dielectric material, a thin layer of gold or silver was sputter coated on the material surface to obtain good images.

The microstructure of ceramics was determined using Scanning Electron Microscope (SEM) (Model JEOL JSM5410). One of the surfaces of the sintered pellets was polished using emery papers of different grades, 1/0, 2/0, 3/0, and 4/0 successively. They were further polished on a velvet cloth using the diamond paste.

SEM micrographs were also observed for fractured as well as etched surfaces. For etching HF acid was applied on the surface of the pellet for a few seconds.

2.6.5 Energy Dispersive X-ray Analysis (EDX)

Energy Dispersive X-Ray Spectroscopy is a microanalytical technique that can be coupled with Scanning Electron Microscopy (SEM). EDX combined with these imaging tools can provide elemental analysis on areas as small as nanometers in diameter. The impact of the electron beam on the sample produces X-rays that are characteristic of the elements found in the sample. When the SEM electron beam bombards the sample, electrons are ejected from the atoms comprising the sample's surface. The resulting electron vacancies are filled by electrons from a higher state, and an X-ray is emitted to balance the energy difference between the two electrons' states. The X-ray energy is characteristic of the element from which it was emitted. This technique determines the elemental composition of individual points or maps out the lateral distribution of elements from selected areas such as grain and grain boundary regions of the ceramics. Chemical compositions and purity of the ceramics were determined by EDX (Model JEOL JSM5410).

2.6.6 Atomic Force Microscopic (AFM) Analysis

Atomic force microscopy is the most versatile and powerful microscopy technology for studying samples at nanoscale. It is versatile in the sense that it can not only image in three-dimensional topography, but it also provides various types of surface measurements to the needs of scientists and engineers. It is powerful because an AFM can generate images at atomic resolution with angstrom scale resolution

height information, with minimum sample preparation. It is applied in three different ways: surfaced sensing, detection and imaging modes.

In surfaced sensing mode, it uses a cantilever with a very sharp tip to scan over a sample surface. As the tip approaches the surface, the close-range, attractive force between the surface and the tip cause the cantilever to deflect towards the surface. However, as the cantilever is brought even closer to the surface, such that the tip makes contact with it, increasingly repulsive force takes over and causes the cantilever to deflect away from the surface.

In detection mode in AFM, a laser beam is used to detect cantilever deflections towards or away from the surface. By reflecting an incident beam off the flat top of the cantilever, any cantilever deflection will cause slight changes in the direction of the reflected beam. A position-sensitive photo diode can be used to track these changes. Thus, if an AFM tip passes over a raised surface feature, the resulting cantilever deflection (and the subsequent change in direction of reflected beam) is recorded by the PSPD.

In imaging mode, an AFM images the topography of a sample surface by scanning the cantilever over a region of interest. The raised and lowered features on the sample surface influence the deflection of the cantilever, which is monitored by the PSPD. By using a feedback loop to control the height of the tip above the surface, thus maintaining constant laser position. The AFM can generate an accurate topographic map of the surface features. The surface morphology was examined by the instrument Atomic Force Microscope (NTEGRA; Prima, U.K.).

2.6.7 Transmission Electron Microscopy (TEM) Analysis

Transmission electron microscopy (TEM) is a microscopic technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as they pass through. An image is formed by the interaction of the electrons transmitted through the specimen, which is magnified and focused onto an imaging device, such as a fluorescent screen.

Bright field TEM images and selected area diffraction patterns (SAED) were obtained by transmission electron microscope (TEM, FEI Tecnai-20G²) equipped with LaB₆ filament with an accelerating voltage of 200 kV. A pinch of fine ceramic powder was dispersed well in acetone using a sonicator. A drop of the solution was

put on a carbon-coated copper grid. After drying acetone from the grid, the sample is ready for TEM analysis through the microscope. TEM micrographs depict nanocrystalline nature of the ceramic. The diffraction pattern has been indexed on the basis of cubic crystal structure for YCTO based ceramics. The additional spots observed in the diffraction pattern are from adjacent grains.

2.6.8 Electric and Dielectric Measurement

The pellets were polished by emery paper (ranges from 0 to 6) and the flat surfaces were coated with Ag paint which was cured at 100 °C for 15 min. The capacitance (C), resistance (R) and dielectric loss ($\tan \delta$) of the cylindrical pellet of the ceramic was measured by the LCR Meter (PSM 1735, Newton 4th Ltd, U.K.) as function of frequency (2 Hz to 5 MHz) in the temperature range 300-500 K with a bias voltage of 1 Volt. The dielectric values of the ceramic materials were calculated from the measured capacitance data. The capacitance, dielectric constant and dielectric loss ($\tan \delta$) can be calculated from the capacitance and conductance measured by equations:

$$C = \epsilon_0 \epsilon_r A / d \quad (2.1)$$

$$\epsilon = \frac{C \times d}{\epsilon_0 A} \quad (2.2)$$

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (2.3)$$

where ϵ stands for the dielectric constant of the dielectric layer, ϵ_0 for the dielectric constant of the free space (8.854×10^{-12} F/m), C is the capacitance (in farad), A is the area (in sq. m) of the electrical conductor and d is the thickness (m) of the dielectric layer.

Dielectric and electrical properties were studied as a function of temperature and frequency to understand the dielectric and electrical behavior of the ceramics. Impedance analysis was carried out to separate the contributions of grains and grain boundaries resistance and capacitance of the materials.

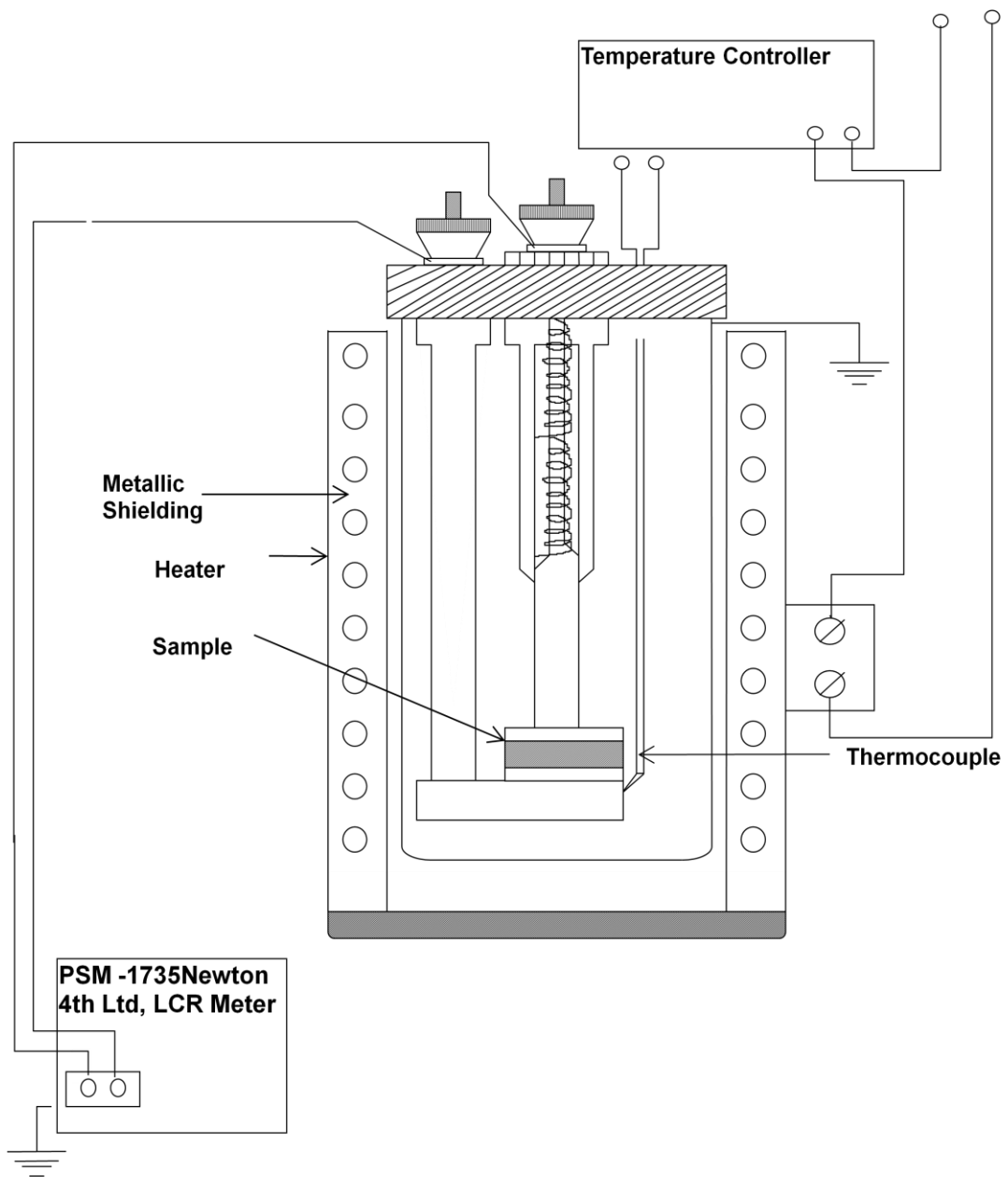


Figure 2.3: Schematic diagram of sample holder assembly used for measurement of dielectric parameters