2.1. Experimental

This chapter explains experimental procedure of nanocomposite ceramic materials. This chapter also includes characterization and application techniques working range of instrument and data recording parameters. The ceramic materials have many interesting properties and improvement of these by materials are synthesized by different route, single phase formation monitor by sintering temperature and time duration and reaction atmosphere. The synthesized ceramic material was characterized to get information about microstructure and particle size. Dielectric, ferroelectric and magnetic properties also investigated at some selected temperature and frequencies. In the present investigation, various samples in different systems were synthesized viz (i) $0.9BaTiO_3–0.1CaCu_3Ti_4O_{12}$ (BTC) (ii) $0.9CaCu_3Ti_4O_{12} – 0.1BaTiO_3$ (CC-BT) (iii) $0.5BaTiO_3–0.5Bi_{2/3}Cu_3Ti_4O_{12}$ (BT-BCT 5) (iv) $0.6Bi_{2/3}Cu_3Ti_4O_{12}$-$0.4BaTiO_3$ (BC-BT) (v) $0.6CaCu_3Ti_4O_{12}$-$0.2Bi_{2/3}Cu_3Ti_4O_{12}$-$0.2Y_{2/3}Cu_3Ti_4O_{12}$ (CBY) synthesized by solid state route. All sample were characterized by various techniques like Powder X-ray diffraction (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX). Dielectric and ferroelectric measurements were carried out by LCR meter respectively at the temperature range of 300- 500K, at some selected frequency. Magnetic measurement performed by MPMS (SQUID magnetometer quantum design) at few selected temperature M-H hysteresis recorded whereas magnetization with temperature (M-T) recorded from 5 – 300K.

2.2. Material used

All synthesized materials involving different elemental compositions have been synthesized by high purity chemicals.

2.2.1 Chemicals

Barium nitrate, Yttrium nitrate, Calcium nitrate, Bismuth nitrate, Copper nitrate Titanium oxide, and citric acid with specification are given bellow in Table.2.1

Table 2.1. Specification of the chemicals used

Raw Materials	**Minimum Assay**	**Manufacturer**
$Ba(NO_3)_2$	99 %	Merk
$Y(NO_3)_3.6H_2O$	99.8%	Sigma-Aldrich
$Ca(NO_3)_2.4H_2O$	99.5%	Merck
$Cu(NO_3)_2.3H_2O$	99.8%	Merck
$Bi(NO_3)_2.4H_2O$	99.5%	Qualigens
TiO_2	99%	Merck
citric acid	99.5%	Merck

2.3. Preparation of materials

The synthesis of materials involves following steps

2.3.1. Preparation of metal nitrate solution

Stoichiometric amount of all metal nitrate (Ba, Y, Ca, Cu and Bi) mentioned in table dissolve in distilled water to make it dissolve completely if required heating solution on hot plate.

2.4. Synthesis methods: The composite ceramic of $0.9BaTiO_3–0.1CaCu_3Ti_4O_{12}$ (BTC), $0.9CaCu_3Ti_4O_{12}–0.1BaTiO_3$ (CC-BT), $0.5BaTiO_3–0.5Bi_{2/3}Cu_3Ti_4O_{12}$ (BT-BCT 5), $0.6Bi_{2/3}Cu_3Ti_4O_{12}$-$0.4BaTiO_3$ (BC-BT), and $0.6CaCu_3Ti_4O_{12}$-$0.2Bi_{2/3}Cu_3Ti_4O_{12}$-$0.2Y_{2/3}Cu_3Ti_4O_{12}$ (CBY) was synthesized by Solid State route. Firstly $Bi_{2/3}Cu_3Ti_4O_{12}$ (BCTO) , YCTO, CCTO, BTO, was synthesized by semi wet route separately.

2.4.1. **Semi wet route**

This route is modified sol-gel technique. It is also named as citrate/glycine-nitrate gel chemical method which is a type of combustion synthesis technique. Combustion synthesis is generally used to obtain multicomponent single phase material. The combustion technique is based on redox reaction between a fuel and oxidant present in the precursor solution. Generally, citric acid, glycine, urea, ethylene glycol etc. are used as a fuel and nitrates of different metals are used as an oxidant. The 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. This leads to the development of porous fluffy ash. Fine phase pure powder can be obtained on further calcination of the ash at high temperature. In semi-wet route developed by us all the metal cations were taken as nitrate except TiO_2 which was taken as solid. Glycine was used as the fuel. 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 metal ions) were added to the solutions. The solution was then heated on a hot plate with magnetic stirrer at 70-80 ^oC 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 porous in nature.

2.4.2. Solid State Route

The perovskite oxides are generally synthesized by conventional solid-state route [13] or dry method. In this route, oxides of various cations with suitable liquid (acetone or ethanol) are mixed in stoichiometric ratio and ground to fine powder using a pestle-mortar. Dried mixed powder is calcined at a particular temperature for a certain period of time. The calcined powder is ground again and converted in to fine powder. An optimum amount of a suitable binder, polyvinyl alcohol (PVA) is added to the powder and mixed uniformly and then it is pressed in to a suitable shape. The resulting product is first heated slowly to a particular temperature to remove the binder and then the temperature of the sample is increased to a particular value and maintained at this value for certain duration for annealing. After annealing, the sample is cooled under controlled rate of cooling. The final resulting product is achieved by diffusion of metal ions at high temperature. Asystematic flow chart is shown in Figure 2.1.

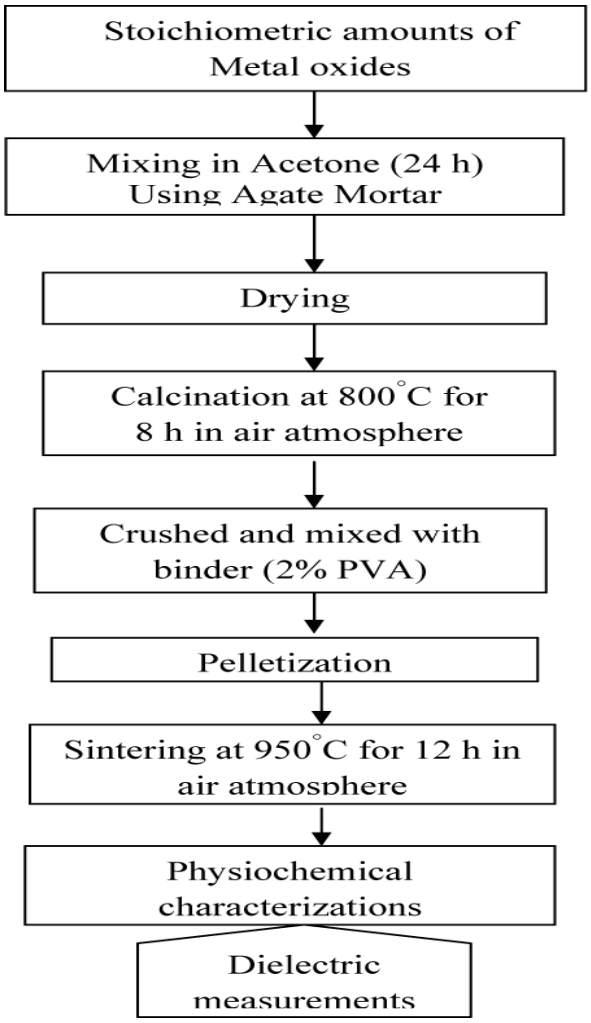

Figure 2.1. Flow chart for the synthesis of materials by solid state route.

2.4.2. Calcination Process

Calcination is a heat treatment process applied to solid powder materials to bring about a thermal decomposition, phase transition, or removal of a volatile fraction. The heat treatment of material in calcination is below melting temperature. The synthesized materials were calcined at 500 °C for 5 hrs and further 800 °C for 8 hrs in a Muffle furnace.

2.4.3 Sintering Process

Sintering is a process of densification of a porous compact by heating it to an appropriate temperature. Mostly cylindrical pellets were prepared on applying pressure and these pellets used

for sintering. In sintering process, solid state reactions and phase change takes place resulting expected compounds.

This ash was calcined in air at 800^{o}C for 8 h in a muffle furnace. The resultant mixtures were ground into fine powder using a pestle and mortar and mixed with few drops of 2% PVA binder. The cylindrical pellets were made using a hydraulic press and were sintered at 1100°C for 12h for dielectric and ferroelectric measurements.

2.5. Characterization techniques for synthesized ceramic materials:

2.5.1. Phase and Crystal Structure Analysis:

X-ray diffraction (XRD) is a powerful technique which gives information about crystalline phases, phase purity, crystallite size and strain state of materials. [Smart and moore (2005), Giacovazzo (2002)] The crystalline materials having three dimensional arrangement of atoms in a particular distance. Crystalline materials have characteristic planes which diffract X-ray in form of peak of particular intensity. The position and intensity of XRD peaks depends upon types of unit cell and atomic position in unit cell. Miller indices is very useful for characterizing unknown materials.

X-ray diffraction spectra of materials were recorded using a MiniFlex600 (Rigaku, Tokyo, Japan) the instrument consists of four components i. e generator, optics, goniometer and detector. In generator, 40kV tube voltage used towards metal target and corresponding tube current is 15mA. The optional graphite monochromator, soller slit (5.0° or 2.5°), and fixed scattering slit are the components of optics. Vertical type goniometer having radius of 150nm working under accuracy of ±0.02°. NaI scintillator and high speed silicon strip detector present in Miniflex600.

Instrument employing Cu-K_α radiation (λ=1.54059 Å). The XRD diffraction patterns recorded at scan rate of 1°/min keeping step size of 0.02.

Figure 2.2. Powder XRD instrument, Rigaku Miniflex600(Japan)

Incident X-ray interact with material and corresponding diffraction observed by atomic plane. If the interplanar spacing (d) is an integer multiple of Xray wavelength, the diffracted Xray constructively interfere. The linear correlation between wavelength and interplanar spacing of solid powder material calculated by Braggs equation written as

$$n\lambda = 2dsin\theta \qquad (2.1)$$

Where n is order of reflection i.e 1, 2, 3, λ represents wavelength of incident radiation, d is the interplaner spacing and θ is Bragg angle.

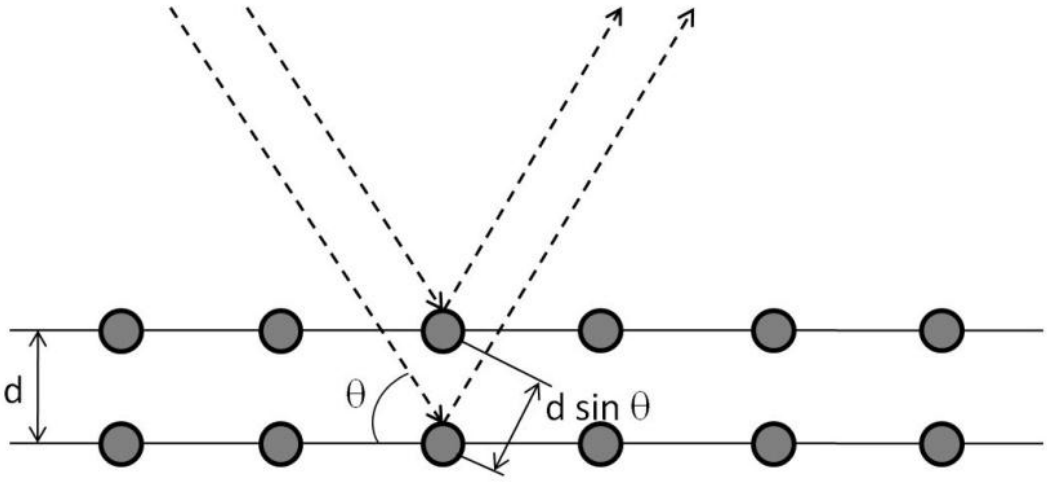

Figure 2.3. Braggs law of difraction

The average crystallite size was calculated by Scherrer formula as given bellow

$$D = \frac{k\lambda}{\beta cos\theta} \qquad (2.2)$$

Where D is the crystallite size (in nm), k represents dimensionless constant (≈0.9), λ is wavelength, β indicates FWHM in radian and θ is diffraction angle.

2.5.3. 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 observed for fractured as well as etched surfaces. For etching HF acid was used on the surface of the pellet for a few seconds.

2.5.4. Energy Dispersive X-ray Analysis (EDX)

Energy Dispersive X-Ray Spectroscopy is a micro analytical 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).

2.5.5. Transmission Electron Microscopy (TEM) Analysis

Transmission electron microscopy (TEM) is a microscopic technique where by 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-20G^2) equipped with LaB_6 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 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 hexagonal perovskite based ceramics.

2.5.6. Atomic force microscopy

The AFM has three major abilities: force measurement, imaging, and manipulation.

In force measurement, AFMs can be used to measure the forces between the probe and the sample as a function of their mutual separation. This can be applied to perform force spectroscopy, to measure the mechanical properties of the sample, such as the sample's Young's modulus, a measure of stiffness.

For imaging, the reaction of the probe to the forces that the sample imposes on it can be used to form an image of the three-dimensional shape (topography) of a sample surface at a high resolution. This is achieved by raster scanning the position of the sample with respect to the tip and recording the height of the probe that corresponds to a constant probe-sample interaction

(see section topographic imaging in AFM for more details). The surface topography is commonly displayed as a pseudocolor plot.

In manipulation, the forces between tip and sample can also be used to change the properties of the sample in a controlled way. Examples of this include atomic manipulation, scanning probe lithography and local stimulation of cells.

Tapping mode Atomic Force Microscope (Bruker, Dimension Edge with Scan Asyst) was used to investigate average roughness and particle size distributions. The rotated cantilevers are designed for high resolution imaging in tapping mode.

2.5.7. Superconducting quantum interference device (SQUID)

The superconducting quantum interference device is one of the most sensitive magnetometers used for magnetic characterization of nanoparticles over a wide range of temperatures and applied magnetic fields [McElfresh (1994)]. The presence of a superconducting coil in SQUID magnetometers requires the employ of liquid helium in order to operate and to determine samples at low temperatures. Magnetic measurements were performed on a superconducting quantum interference device (SQUID) (Quantum Design, MPMS 3). Field-dependent magnetization curves were obtained in the temperature range 5-300 K up to a maximum field of 7 T. Two kinds of measurements were performed, temperature-dependent magnetization curves were recorded under zero field cooled (ZFC) and field cooled (FC) conditions from 2 to 300 K under an applied field of 500 Oe.

2.5.8. 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 $^{\circ}$C for 15 min. The capacitance (C), resistance (R) and

dielectric loss (tan δ) of the cylindrical pellet of the ceramic was measured by the LCR Meter named PSM 1735, Newton 4th Ltd, U.K. as function of frequency (100 Hz to 5 MHz) in the temperature range 300-500 K with a bias viltage 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 δ) can be calculated from the capacitance and conductance measured by equations:

$$C = \varepsilon_0 \varepsilon_r A / d \tag{2.1}$$

$$\varepsilon = \frac{C \times d}{\varepsilon_0 A} \tag{2.3}$$

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \tag{2.4}$$

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**.**

2.5.9. Impedance and Conductivity

The simple resistor–capacitor (RC) equivalent circuit and the modified constant phase element (CPE) circuit were used to describe the impedance spectroscopy, and excellent agreement between the calculated and measured curves was obtained in the CPE circuit. The resistance and

capacitance of the grains and grain boundaries can be tuned by changing the annealing atmosphere and temperature. Under an oxygen absent annealing atmosphere, the electric resistances of the grain boundaries changed greatly but the resistance of the grains showed almost no change. While under an oxygen annealing atmosphere, the reverse process occurred. On the basis of this result, it is demonstrated that the origin of the semi conductivity of the grains in composite polycrystalline films arises from their oxygen-loss, while the grain boundaries are close to oxygen-stoichiometry.