2.1. Experiment

This chapter describes the experimental procedure for synthesis of Bismuth Copper Titanium oxide ($Bi_{2/3}Cu_3Ti_4O_{12}$) and Bismuth Lanthanum Titanium oxide ($Bi_3LaTi_3O_{12}$) ceramics and their composite materials. Many different physiochemical techniques were used for their characterization. Materials research in the area of electro ceramic involves (1) Synthesis of various compositions in the system, (2) Heat treatment at high temperature, (3) Crystal phase analysis and (4) Micro structural properties, (5) Dielectric and magnetic behavior of prepared ceramic and composite materials. In the present investigations (a) $Bi_{2/3}Cu_3Ti_4O_{12}$ (BCTO) (b) $Bi_3LaTi_3O_{12}$ (BLTO) were prepared by Semi-wet route and also characterized synthesized the following composites (a) 0.5 $Bi_{2/3}Cu_3Ti_4O_{12}$ - 0.5 $Bi_3LaTi_3O_{12}$ (BCLT-55) (b) 0.9 $Bi_{2/3}Cu_3Ti_4O_{12}$ - 0.1 $Bi_3LaTi_3O_{12}$ (BCLT-91) (c) 0.9 $Bi_3LaTi_3O_{12}$ - 0.1 $Bi_{2/3}Cu_3Ti_4O_{12}$ (BCLT-19) by variation of compositions of two parent ceramics.

For the synthesis of various compositions in the above system, we have used high purity raw materials viz: Calcium nitrate, lanthanum oxide, copper nitrate, bismuth nitrate, titanium di oxide and citric acid with specification given in table 2.1.

Table 2.1. The chemicals used for synthesis of BCTO, BLTO and their composites.

Raw Materials	Minimum Assay	Manufacturer
Bismuth nitrate, $Bi(NO_3)_3.5H_2O$	99.5%	Merck, India
Copper nitrate, $Cu(NO_3)_2.3H_2O$	99.8%	Merck, India
Solid lanthanum oxide, La_2O_3	99.0%	Merck, India
Titanium oxide, TiO_2	99.9%	Merck, India
Citric acid, $C_6H_8O_7.H_2O$	99.5%	Merck, India

2.2. Synthesis of Materials

a) **Semi-wet Route**

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

b) **Preprartion of Ceramic Material**

In this route, 0.1 molar standard nitrate solutions of each of Bismuth (Bi), Copper (Cu). Lanthanum oxide (La_2O_3), titanium oxide (TiO_2) were taken in stoichiometric molar ratio. Solutions of $Bi(NO_3)_3.5H_2O$ was prepared using distilled water and La_2O_3 dissolved in dil. nitric acid. Both the solution was mixed in a beaker. Solid TiO_2 in powder form was added to the solution. A calculated amount of citric acid equivalent of the metal ions was dissolved in water and also added in the heterogeneous mixture. The heterogeneous mixture was heated on a hot plate using magnetic stirrer at 70-80 ℃ to evaporate water. The residual mass was dried at 100-120 ℃ in hot air oven. The ash was calcined at 800 ℃ for 6 h in a muffle furnace and then achieved sample was ground into a fine powder using a mortar and pestle. Cylindrical pellets (11.6 mm x 1.00 mm) were made using a hydraulic press applying pressure of 4 tons for 1 min.

The pellets were sintered at 900 °C for 8 h for dielectric and magnetic behavior measurement. A flow chart showing the various steps in the preparation of these materials by this method is shows in figure 2.1.
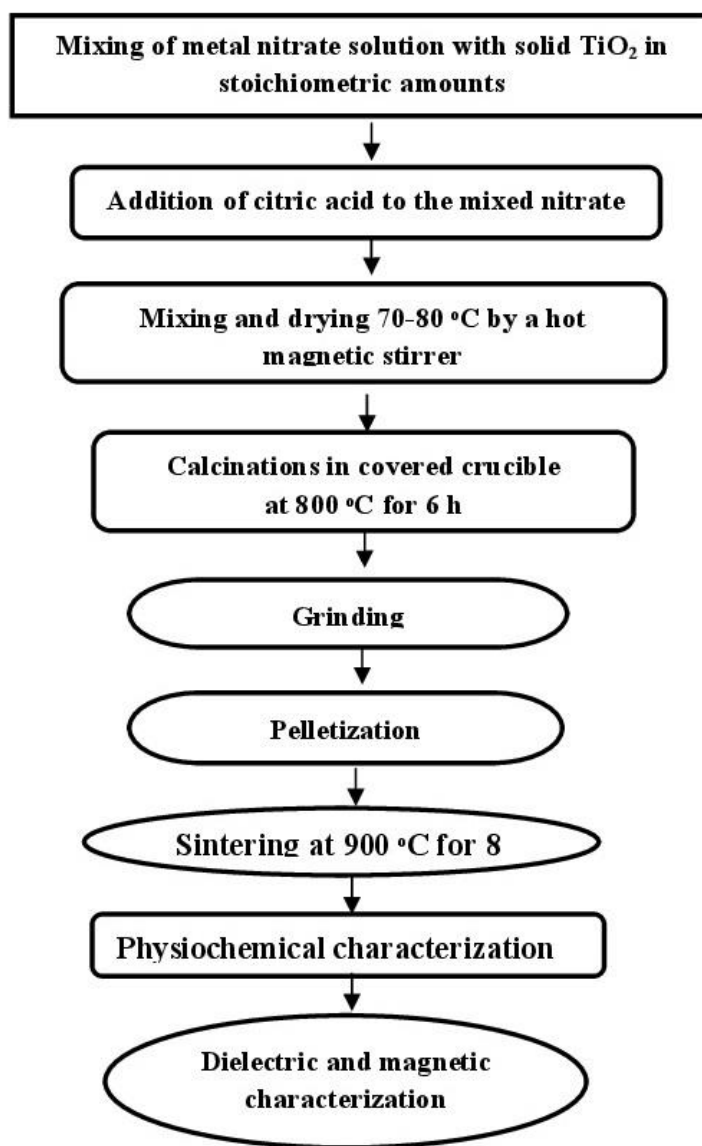

Fig. 2.1. Flow chart for the synthesis of complex perovskite by the semi-wet route.

c) Preparation of Composite Materials

The Prepared and calcined ceramic materials of BCTO and BLTO were take an appropriate amount and mixed with ethanol and ground for 24 h in ports in a mortar and pastel to make a uniform dispersion of the composite. The obtained composite powder was used to make cylindrical pellets on applying 4-5 tons of pressure using 2-3 drops of 2% poly vinyl alcohol (PVA) as a binder. The pellets were pre heated to 500 °C for 2 h to remove the binder and finally sintered at 900 ºC for 8 h. The sintered pellets were used for further different characterizations. A flow chart for synthesis of composite was shown in Figure 2.2.

2.3. Calcination Process

➢ Calcination is a heat treatment process applied to solid materials to bring about a thermal decomposition, phase transition of removal of a volatile fraction. The heating is operating below the melting point of the product materials.

➢ Calcination is also used to mean a thermal treatment process in the absence or limited supply of air or oxygen applied to ores and other solid materials to bring about a thermal decomposition.

2.4. Sintering Process

The calcined powder was transferred to an agate mortar and ground in to fine powder. A few drops of 2% poly vinyl alcohol were added and mixed well with the powder. Powder was pressed in to cylinder pallets (10 mm x 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 hours to burn off the binder completely.
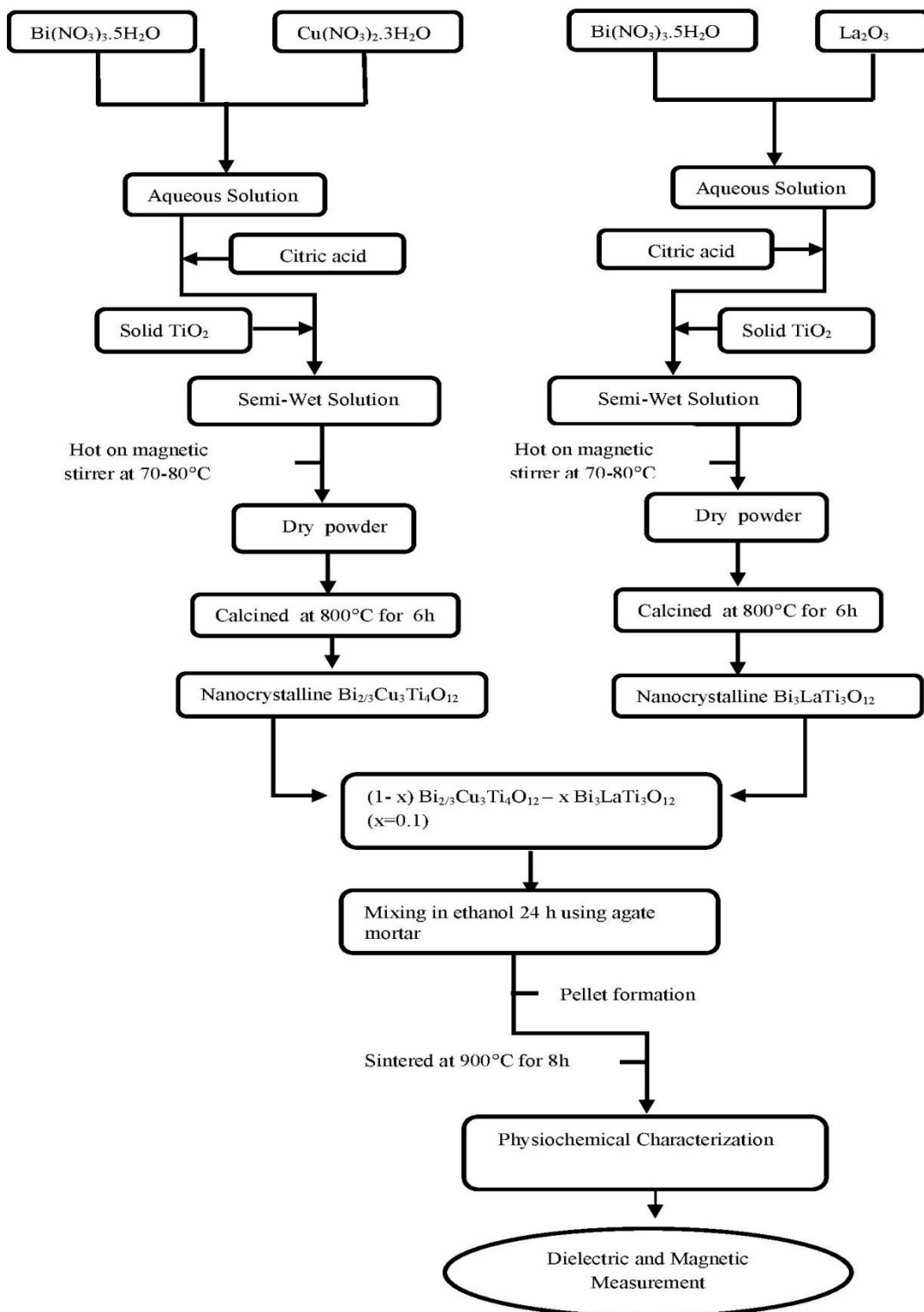

$Bi(NO_3)_3.5H_2O$	$Cu(NO_3)_2.3H_2O$		$Bi(NO_3)_3.5H_2O$	La_2O_3

Aqueous Solution

Citric acid

Solid TiO_2

Semi-Wet Solution

Hot on magnetic stirrer at 70-80°C

Dry powder

Calcined at 800°C for 6h

Nanocrystalline $Bi_{2/3}Cu_3Ti_4O_{12}$

Aqueous Solution

Citric acid

Solid TiO_2

Semi-Wet Solution

Hot on magnetic stirrer at 70-80°C

Dry powder

Calcined at 800°C for 6h

Nanocrystalline $Bi_3LaTi_3O_{12}$

$(1- x)\ Bi_{2/3}Cu_3Ti_4O_{12} - x\ Bi_3LaTi_3O_{12}$ (x=0.1)

Mixing in ethanol 24 h using agate mortar

Pellet formation

Sintered at 900°C for 8h

Physiochemical Characterization

Dielectric and Magnetic Measurement

Fig.2.2. Flow chart for the synthesis of the composites by semi-wet route.

Sintering is a process of densification of a porous compact by heating it to an appropriate temperature. These pellets were maintained at their respectively sintering temperature 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. The pellets were maintained at 900 °C temperature for 8 h.

2.5. X-Ray Diffraction Analysis

X–ray diffraction (XRD) is powerful technique used primarily for crystallographic characterization of solid materials, based on the basic principal that the angle of reflection of X-rays form a sample that related to the crystal structure and composition of the materials and thin film, and also the composition of crystallographic phases present in a sample. The sintered pallets were ground and powder X–ray diffraction pattern were recorded using an X-ray diffractometer (Rigaku miniflex 600, Japan) with Cu-K_α, radiation (λ = 1.54 Å) at scanning rate of 2°/min. The phase formation of solid materials was confirmed by the absence of characteristics lines of constituent oxides or any other compound between them in the XRD pattern. The XRD pattern was indexed and lattice parameter determined using least square fitting of the data using a software program 'CEL'. The X-ray analysis was performed by the usual Hanawanlt's method of the comparative peak matching with the standard Joint Committee on Powder Diffraction Standards (JCPDS) files. The 'd' spacing is calculated for different samples from the diffraction data obtained using Bragg's law. The 'd' value matched with those exiting in JCPDS files for the identification of different phases. The X-ray analysis has been made the most popular method for the estimation of crystalline size in nano phase materials and therefore has been extensively used in the present work.

Fig.2.3. Powder X-ray diffractrometer, Rigaku Miniflex600 (Japan).

The broadening of the Bragg's peaks have been ascribing to crystalline size refinement, instrumental broadening and strain broadening. The average crystallite size was calculated using line broadening method. The Cauchy component and Voigt function represent the crystallite size for single-line analysis method. The crystallite size of the ceramics was determined by Debye-Scherrer formula.

$$D = k\lambda/\beta \cos\theta \qquad (2.1)$$

where D is the crystallite size, λ is the wavelength of X-ray, k is a constant taken as 0.89, θ is the Bragg angle of the peaks and β is the full width at half maximum (FWHM) of the peak.

2.6.FT-IR Spectroscopy

Fourier transform Infrared (FT-IR) spectra was recorded using ATR-FTIR spectrophotometer (Bruker, ALPHA model) in the range from 4000 cm^{-1} - 500 cm^{-1}. The sample was mixed with solid KBr, then ground and pressed into a pellet using a hydraulic press. An average of 64 scans with 4 cm^{-1} resolution was recorded for each sample.

2.7.Transmission Electron Microscopy (TEM) Analysis

Transmission electron microscopy (TEM) is a microscopic technique where a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as they pass through.

Fig.2.4. Transmission Electron Microscope (TEM, FEI TECANI G^2 20 TWIN, USA) used to determining particle structure.

An image is formed from 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, selected area diffraction patterns (SAED) and the high-resolution TEM (HR-TEM) images were obtained by transmission electron microscope (TEM, FEI TECANI G^2 20 TWIN, USA) equipped with LaB_6 filament with an accelerating voltage of 200 kV. For this purpose, the fine powder of the ceramic was dispersed in acetone using a sonicator. A drop of the solution was added on a carbon-coated copper grid. After drying acetone form the copper grid, the grid was observed under the microscope.

TEM micrographs depict nano-crystalline nature of the ceramic. The electron diffraction pattern and HR-TEM has been indexed on the basis of complex perovskite based ceramics and composites.

2.8. 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 grains and the size of grains. 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 coated on the surface of the material surface in order to obtain good images.

Fig.2.5. Scanning Electron Microscope (ZEISS, model EVO-18 Research) used for microstructure of the surface of the ceramics.

Microstructure of ceramics was determined using Scanning Electron Microscope (SEM) (ZEISS, model EVO-18 Research; Germany). One of the surfaces of the sintered pellets was polished using emery papers of different grades 0/0, 1/0, 2/0, 3/0, 4/0, and 5/0 successively. They were further polished on a velvet cloth using gold paste of the order 1µm and 1/4µm followed by thermal etching. In some cases, microstructural studies are carried out for fractured surfaces of the sintered pellets.

2.9. Energy Dispersive X-ray (EDX) Analysis

Energy Dispersive X-Ray Spectroscopy is a micro-analytical technique that can be coupled with Scanning Electron Microscopy (SEM) or Transmission Electron Microscope (TEM). 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 sample is bombarded by the SEM electron beam, 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 (ZEISS, model EVO-18 Research; Germany).

2.10. Atomic Force Microscopy (AFM) Analysis

Tapping mode Atomic Force Microscope (NTEGRA Prima, Germany) was used to investigate average roughness and particle size distributions. The rotated cantilevers are designed for high resolution imaging in tapping mode.

2.11. Superconducting Quantum Interference Device (SQUID)

Magnetic measurements were performed on a superconducting quantum interference device (SQUID) (Quantum Design, MPMS 3).The superconducting quantum interference device is one of the most sensitive magnetometers used for magnetic characterization of nano particles over a wide range of temperatures and applied magnetic fields. The presence of a superconducting coil in SQUID magnetometers requires the employ of liquid helium in order to operate and to determine magnetic properties of the samples at low temperatures. 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 2-300 K under an applied field of 100 Oe.

2.12.   Electric and Dielectric Measurement

The sintered pellets were polished by emery paper (ranges from 0 to 6) and the flat surfaces were coated with silver paint which was cured at 100 $^\circ$C for 15 min. The capacitance (C), resistance (R), dielectric loss (tan δ) and real impedance (Z′) of the cylindrical pellet of the ceramic was measured by the LCR meter (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 voltage of 1 Volt. The dielectric values of the ceramic materials were calculated from the measured capacitance data.
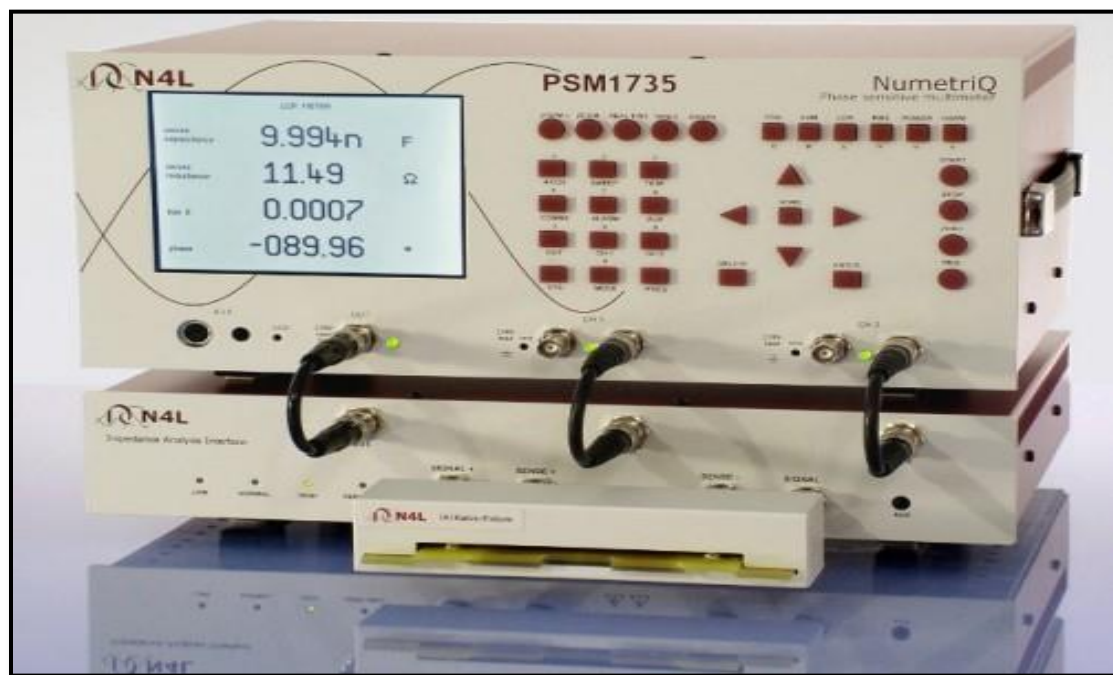

Fig.2.6. LCR meter (PSM 1735, Newton 4th Ltd, U.K.) used for dielectric properties measurement.

The relative dielectric constant (ε_r) can be calculated from the measured value as per equation given below:

$$\varepsilon_r = \frac{C \times d}{\varepsilon_0 A} \qquad (2.2)$$

where 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 (in 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.