CHAPTER – 2

Synthesis and Characterization Techniques

2.1. Experiment

This chapter describes the experimental procedure for the synthesis of Calcium Copper Titanium oxide $CaCu_3Ti_4O_{12}$, Calcium Copper Manganese Oxide ($CaCu_3Mn_4O_{12}$), and Mn-doped CCTO ceramic Copper site, Titanium site and simultaneously. Many different physiochemical techniques were used for their characterization. The ceramics were to be synthesized and characterized. (1) Synthesis of various compositions in the system, (2) Heat treatment at high temperature, (3) Crystal phase analysis, and (4) Microstructural properties (5) Oxidation state (5) Dielectric studied (6) Magnetic properties studied of all; the ceramics.In the present investigations (a) $CaCu_3Ti_4O_{12}$ (CCTO) (b) $CaCu_{2.9}Mn_{0.1}Ti_{3.9}Mn_{0.1}O_{12}$ (CCMTMO), $CaCu_2Mn_1Ti_4O_{12}$ (CCMTO) ,$CaCu_3Ti_{3.9}Mn_{0.1}O_{12}$(CCTMO) (Semi-wet Route), $CaCu_3Mn_4O_{12}$ (CCMO) (Chemical method) .

All the ceramics were to be synthesized through a semi-wet route but CCMO ceramic was synthesized through a chemical route. For the synthesis of all ceramic high purity raw materials viz: Calcium nitrate, copper nitrate, titanium dioxide, and citric acid, Manganese acetate with the specification given in table 2.1.

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

Raw Materials	**Minimum Assay**	**Manufacturer**
Calcium Nitrate $Ca(NO_3)_2{\cdot}4H_2O$	99.2%	Merck, India
Copper nitrate, $Cu(NO_3)_2.3H_2O$	99.8%	Merck, India
$Mn(CH_3COO)_2{\cdot}4H_2O$	99.0%	Merck, India

(Magneese acetate)		
Titanium oxide, TiO_2	99.9%	Merck, India
Glycine (NH_2-CH_2-COOH)	99%	Merck, India

2.2. Synthesis of Materials

a) Semi-wet Route

Standard solutions of metal nitrates were prepared using distilled water as mentioned above. Solutions of metal nitrates in stoichiometric amounts were mixed in a beaker. Stoichiometric amounts of solid TiO_2 and glycine (equivalent to metal ions) were added to the solutions. The solution was heated on a hot plate magnetic stirrer at 70-80 °C to evaporate water followed by drying at 100-120°C in a hot air oven for 12 hrs to yield a blue gel.

(b) Chemical method

In this method, all-metal nitrate are dissolved in double-distilled water in the required amount in the beaker and chelating like citric acid, glycine etc in stoichiometric amount.

2.3Calcination Process:

Calcination is a thermal treatment process applied to solid materials to bring about a thermal decomposition, phase transition, or removal of a volatile fraction. The calcination process normally takes place at temperatures below the melting point of the product materials. The gel was calcined in air at 800 °C for 6 hrs in an electrical furnace. After calcination, an ash-type mass was obtained.

2.4 Pressing and Sintering of Samples: The calcined powder was transferred to an agate mortar and ground to form a powder. A few drops of 3% polyvinyl alcohol were added and mixed well with the powder. Powders were pressed into cylindrical pellets by using a hydraulic press. These pellets were kept in a platinum crucible, covered with a platinum lid and heated slowly to 600℃ for 8 h, and kept at this temperature for about two hours to burn off the binder completely. Sintering is a process for densification of a porous compact by heating it at the 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 900 ℃ temperatures for 8 hours. A flow chart showing the various steps for the preparation of these materials by this method is shown in the figure 2.1.

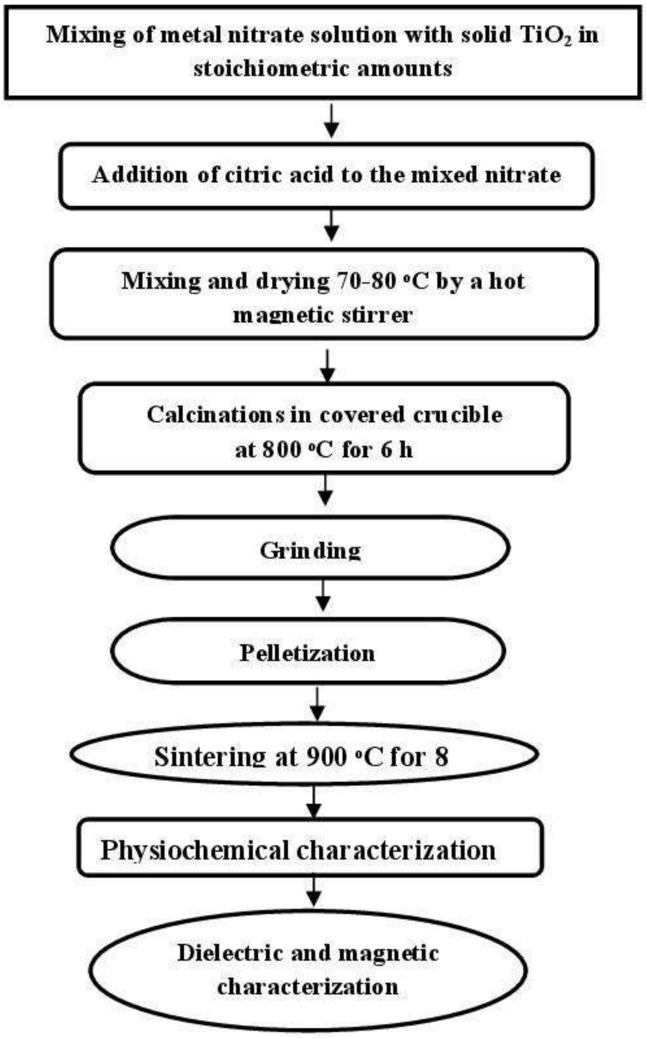

Figure 2.1. Flow chart for the synthesis of complex perovskite by the semi-wet route.

2.5. X-Ray Diffraction Analysis

Phase Formation and Crystal Structure Determination: X-ray diffraction (XRD) is a powerful technique used primarily for crystallographic characterization of solid materials, based on the basic 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 composition of crystallographic phases present in a sample. The sintered pellets were ground and powder x-ray diffraction patterns were recorded using an X-ray Diffractometer (Rigaku

Miniflex600 (Japan) employing Cu-KαI radiation (λ~ 0.154 nm). The formation of a single-phase solid solution was confirmed by the absence of characteristic lines of constituent oxides or any other compounds between them in the XRD patterns. The XRD patterns were indexed and lattice parameters were determined using the least square fitting of the data using a software program 'Cel'.

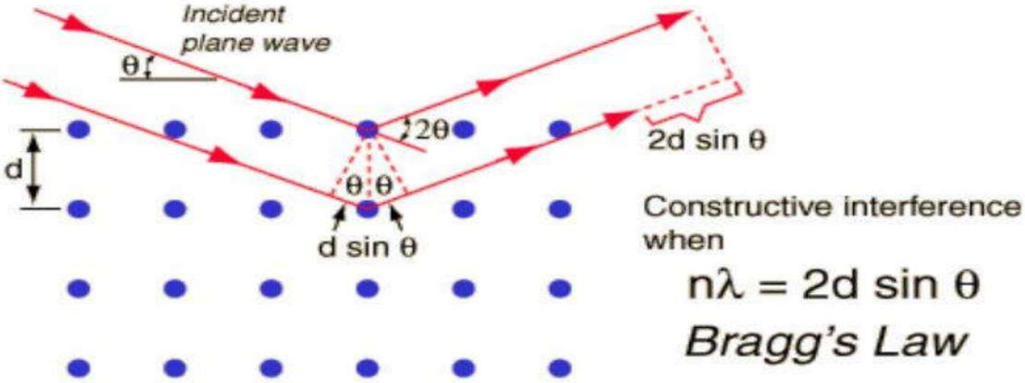

Figure 2.2. shows the basic concept of X-ray diffraction pattern.

Figure 2.3. Powder X-ray diffractometer, Rigaku Miniflex600 (Japan).

Crystalline size refinement, instrumental widening, and strain broadening have all been blamed for the expansion of Bragg's peaks. Using the line broadening approach, the average crystallite size was estimated. For the single-line analysis method, the crystallite size is represented by the Cauchy component and Voigt function. The Debye-Scherrer formula was used to determine the crystallite size of the ceramics.

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

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 transforms infrared (FT-IR) spectra were acquired in the range of 4000 cm-1 to 500 cm-1 using an ATR-FTIR spectrophotometer (Bruker, ALPHA model). The material was crushed and compacted into a pellet using a hydraulic press after being combined with solid KBr. Each sample received an average of 64 scans with a resolution of 4 cm^{-1}

2.7. Microstructural Studies (SEM):

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals derived 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 characterization, the cross-section of samples was polished before observation. For non-conductive dielectric samples, a thin layer of gold was sputter-coated on the sample surface to obtain good images. For microstructural studies, sintered pellets were polished using emery papers of grade 0/0, 1/0, 2/0, 3/0, 4/0, and 5/0 successively. One of the polished pellets is further polished on a velvet cloth with the diamond paste of the order 1µ and 1/4µm. For microstructural studies, the pellets were fractured, and then, they were thermally etched. The micrographs were recorded using, (Model JEOL JSM5410) scanning electron microscope (SEM).

2.8 Energy Dispersive X-ray Spectroscopy (EDX): Energy Dispersive X-Ray Spectroscopy (EDX) is a chemical microanalysis technique used in conjunction with scanning electron microscopy (SEM). EDX technique detects x-rays emitted from sample 43 during bombardment by an electron beam to characterize the elemental composition of the analyzed volume. Features or phases as small as 1 µm or less can be analyzed. 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.

Figure 2.4. Scanning Electron Microscope (ZEISS, model EVO-18 Research) used for microstructure of the surface of the ceramics.

2.9.Transmission Electron Microscopy (TEM):

Transmission electron microscopy (TEM) is a microscopy 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 from the interaction of the electrons transmitted through the specimen, which is magnified and focused onto an imaging device, such as a fluorescent screen, as is common in most TEM. A Philips CM200 equipped with LaB6 filament operated at 200 KV high-resolution transmission electron microscope (HRTEM) was also used to analyze the particle size of core-shell particles and the thickness of the shell layer operating at 400 KV. The Philips CM200 equipped with LaB6 filament operated at 200 KV has a point-to-point image resolution of 0.18 nm, and it uses a top-entry specimen stage for high mechanical stability. Spatially resolved EDX attached with the HRTEM was used to confirm the presence and element composition of a thin layer of shell around the nanoparticles after surface modification. TEM micrographs depict finer grain size. The diffraction pattern has been indexed on the basis of cubic crystal structure. The additional spots observed in the diffraction pattern are from adjacent grains. If the particle size observed by TEM are not in agreement with results determined by XRD and SEM. The error in the particle sizes obtained from the XRD results is large, and the average values obtained from SEM are significantly larger than that obtained from XRD. These differences could be resulted from some dispersion 44 or inhomogeneity in the particle size of the samples. Electron diffraction of particles with higher calcination temperature contains more intense spots.

Figure 2.5. Transmission Electron Microscope (TEM, FEI TECANI G^2 20 TWIN, USA) used to determine particle structure.

2.10.X-ray Photoelectron Spectroscopy (XPS): X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a sensitive non-destructive analysis technique for the elemental composition and chemical state of the top 5 to 100 Å of a surface with a sensitivity of 0.1% of a monolayer.5 It operates on the basic principle as X-ray irradiation of sample results in the emission of photoelectrons whose energy is related to the binding energy of the electrons, providing elemental and chemical state information of the specimen. In this study, XPS was employed to investigate the surface chemistry characteristics of the Ag nanoparticles. XPS analysis was performed on a Model Omicron Nanotechnology X-rays from an Mg K-alpha source (1253.6 eV) with spectrometer resolution ~1.0 eV for survey scans and ~0.1 eV for high-resolution scans. It is equipped with an electron flood gun to neutralize charge build-up and an Argon ion gun to etch and clean samples for depth profiling.

2.11.Raman spectroscopy

Raman spectroscopy is a non-destructive chemical analysis technique that can reveal information on chemical structure, phase and, crystallinity, polymorphy and molecular interactions. It is based on light's interaction with a material's chemical bonds.

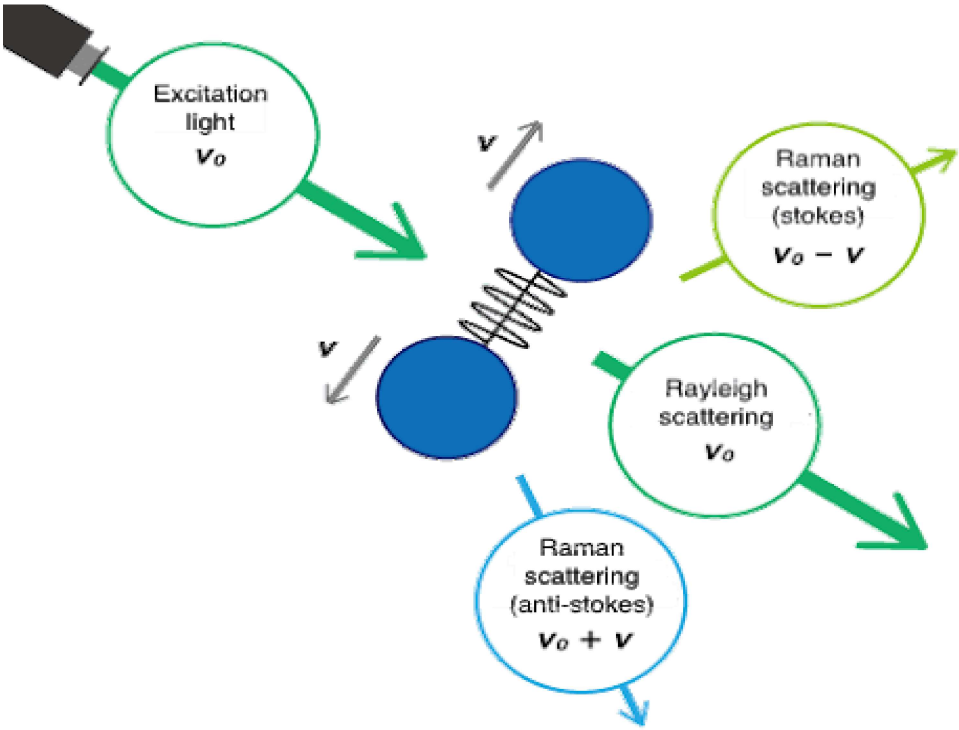

Figure 2.6. The basic principle of Raman spectroscopy

2.12.Atomic Force Microscopy (AFM) Analysis

Mode of tapping the average roughness and particle size distributions were investigated using an atomic force microscope (NTEGRA Prima, Germany). In tapping mode, the rotating cantilevers are optimized for high-resolution imaging.

2.13.Quantum Interference Device (SQUID)

A superconducting quantum interference device (SQUID) was used to conduct magnetic measurements (Quantum Design, MPMS 3). One of the most sensitive magnetometers for magnetic characterization of nanoparticles over a wide range of temperatures and applied magnetic fields is the superconducting quantum interference device. The inclusion of a superconducting coil in SQUID magnetometers necessitates the use of a superconducting coil. the use of liquid helium to operate and evaluate the magnetic characteristics of samples at low temperatures In the temperature range of 5-300 K, field-dependent magnetization curves were obtained up to a maximum field of 7 T. Temperature-dependent magnetization curves were recorded under zero-field cooled (ZFC) and field cooled (FC) conditions from 2-300 K under a 100 Oe applied field in two different ways.

2.13.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 0C for 15 min. capacitance (C) and dielectric loss (D) were measured using a PSM 1735, Newton 4th Ltd, U.K as a function of frequency (100 Hz –1 MHz) in the temperature range 300-500K with a bias voltage of 1Volt.

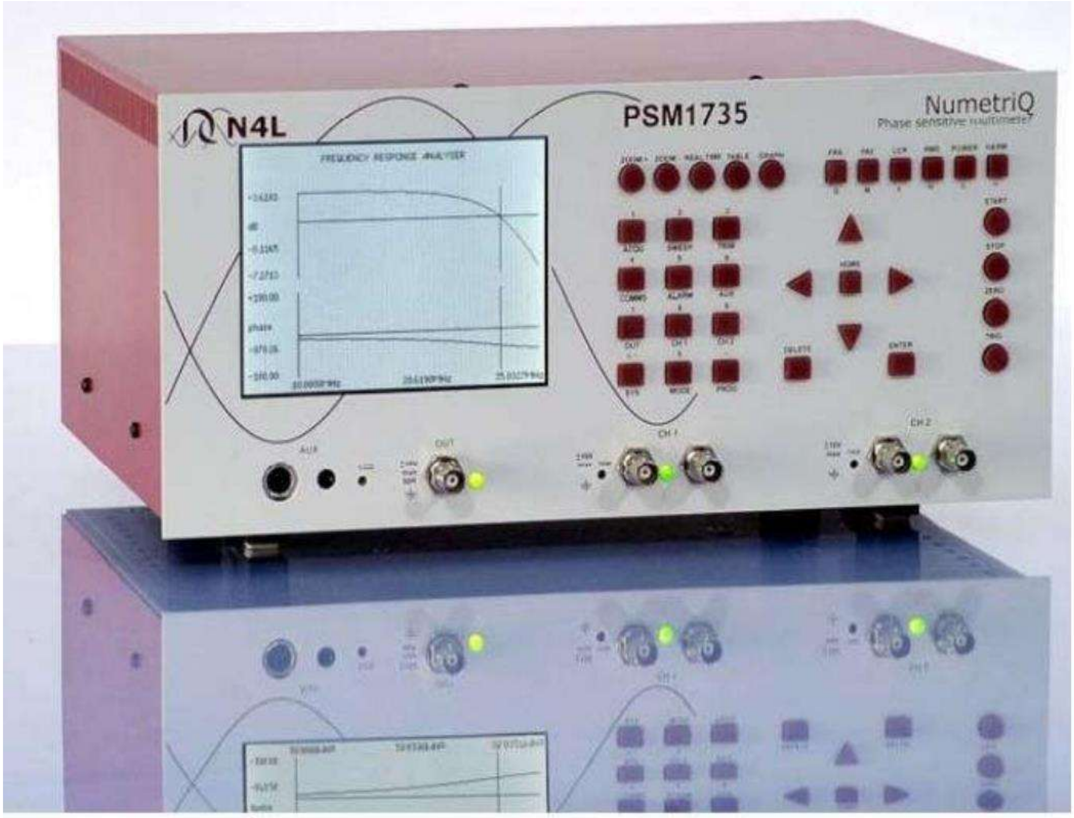

Figure2.7. LCR meter (PSM 1735, Newton 4th Ltd, U.K.) used for dielectric properties measurement.

The dielectric constant (ε_r) of all the ceramic were examined by using following given below equation

$$\varepsilon_r = \frac{C \times d}{\varepsilon_0 A} \tag{2.2}$$

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 mm) of the dielectric layer.

The dielectric constant of all ceramic were to be examined by dielectric constant versus temperature and frequency,tangant loss against temperature and frequency. The contributions of grains and grain boundaries resistance and capacitance of the materials was analyzed by impedance spectroscopy.