CHAPTER – 2

Synthesis and Characterization Techniques

2.1. Experimental

This chapter explains experimental procedure of complex perovskite 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 is 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 behavior also investigated at some selected temperature and frequencies. In the present investigation, various samples in different systems were synthesized

(i) $CaCu_3Ti_4MnO_{12}$ (CCTMO) (ii) $CaCu_3Ti_{3.5}Mn_{0.5}O_{12}$ (iii) $CaCu_3Ti_{3.75}Mn_{0.25}O_{12}$

(iv) $CaCu_3Ti_{3.5}W_{0.5}O_{12}$ (CCTWO) (v) $CaCu_3Ti_{3.5}Nb_{0.5}O_{12}$ (CCTNO) synthesized through semi-wet route. All samples 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 – 300 K.

2.2. Material used

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

2.2.1 Chemicals

Calcium nitrate, Copper nitrate, Manganese acetate, Tungston dioxide, Niobium pentoxide, 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**
$Ca(NO_3)_2.4H_2O$	99.5%	Merck
$Cu(NO_3)_2.3H_2O$	99.8%	Merck
$Mn(CH_3COO)_2.4H_2O$	99.0%	Merck
WO_2	99.0%	Merck
Nb_2O_5	99.0%	Merck
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 (Ca, Cu), acetate of Mn, and oxide of (Nb and W) mentioned in table dissolve in double distilled water to make it dissolve completely if required heating solution on hot plate.

2.4. Synthesis methods:

The complex perovskite $CaCu_3Ti_4MnO_{12}$ (CCTMO), $CaCu_3Ti_{3.5}Mn_{0.5}O_{12}$, $CaCu_3Ti_{3.75}Mn_{0.25}O_{12}$, $CaCu_3Ti_{3.5}W_{0.5}O_{12}$ (CCTWO), $CaCu_3Ti_{3.5}Nb_{0.5}O_{12}$ (CCTNO) successfully synthesized through semi-wet route.

2.4.1. Semi wet route

This route is a technique modified to sol-gel. It is also referred to as a chemical method of the citrate/glycine-nitrate gel which is a type of technique for combustion synthesis. Combustion synthesis is generally used to obtain single-phase material in multi-components. The combustion technique is based on the redox reaction present in the precursor solution between a fuel and oxidant. Citric acid, glycine, urea, ethylene glycol etc. are generally used as a fuel, and as an oxidant are used nitrates of different metals. In the precursor solution, chelating agents such as EDTA, acetic acid, etc. can form complex with metal ions and act as fuel. This complex, on dehydration, produces a viscous gel that auto-ignites with the evolution of enormous quantities of gases when further heated. That leads to porous fluffy ash developing. Pure fine phase powder can be obtained at high temperature on further ash calcination.

All of the metal cations were taken as nitrate in semi-wet route developed by us except for TiO_2 which was taken as solid. Glycine was used as the gasoline. Solutions of metal nitrates were combined in a beaker in stoichiometric quantities. To the solutions were added stoichiometric amounts of solid TiO_2 and aqueous glycine solution (equivalent to metal ions). The solution was then heated up to evaporate water on a hot plate with a magnetic stirrer at 70-80 ^oC. During heating, dehydration of the homogeneously mixed solution caused a gel to form. This gel followed by its swelling on further heating of self-ignites. This ash produced for the ignition was porous in nature.

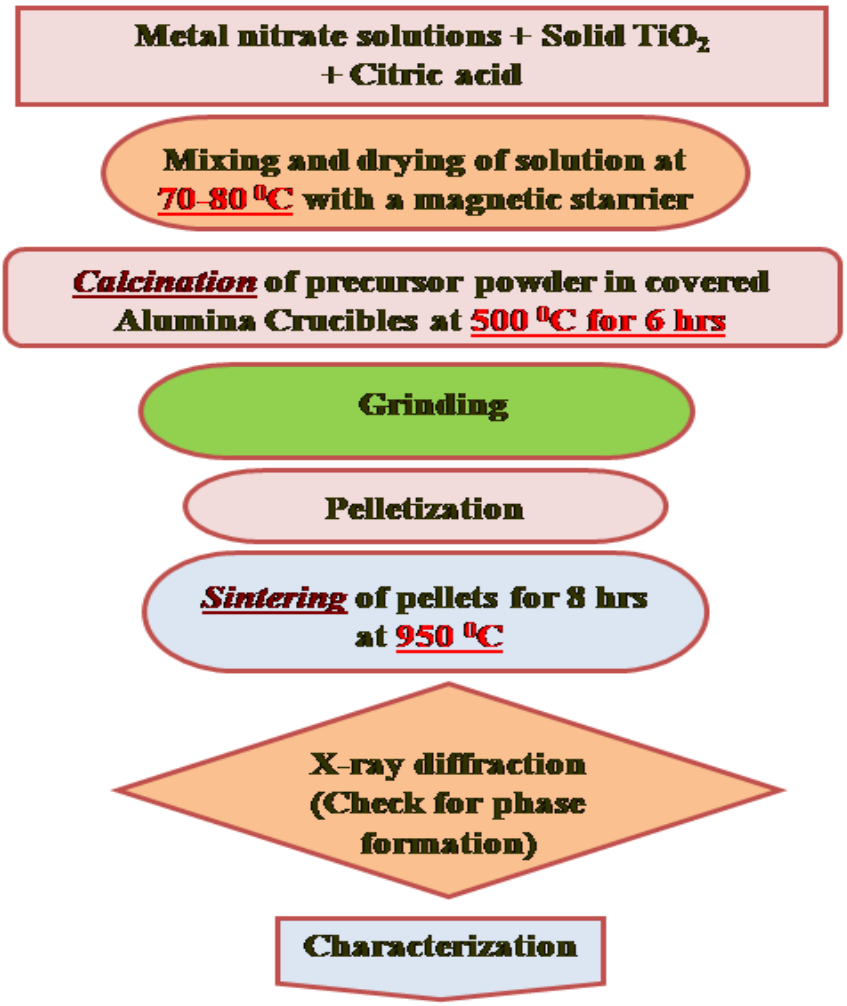

Figure 2.1. Flow chart for the synthesis of materials by semi-wet route

2.4.2. Solid State Route

In general, perovskite oxides are synthesized using conventional solid-state route or dry method. Oxides of various cations with suitable liquid (acetone or ethanol) are mixed using a pestle-mortar in stoichiometric proportion and ground to fine powder in this route. For a certain period of time, dried mixed powder is calcined at a given temperature. The calcinated powder is reduced to fine powder and ground again. An optimal quantity of an effective binder, polyvinyl alcohol (PVA) is applied to the powder and mixed evenly and then pressed into the appropriate form. The resulting product is first heated slowly to a specific temperature to remove the binder, and then the sample temperature is increased to a specific value and maintained for certain duration at this value for annealing. The sample is refrigerated under controlled cooling rate after annealing. The end resulting product is accomplished by high-temperature diffusion of metal ions. Figure 2.1 displays a systematic flow diagram.

2.4.2. Calcination Process

Calcination is a heat treatment process that is applied to solid powder materials to cause a thermal decomposition, phase transition, or removal of a volatile fraction. Material heat treatment in calcination is below the temperature of melting. The synthesized materials were calcinated in a Muffle furnace at 500 ^{o}C for 5 hours and 800 ^{o}C further for 8 hours.

2.4.3 Sintering Process

Sintering is a process of densifying a porous compact, heating it to a suitable temperature. Mostly cylindrical pellets were prepared on applying pressure and these

pellets used for sintering. Solid state reactions and phase change occur during the sintering process resulting in the 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 that provides information on crystalline phases, phase purity, crystallite size and material strain state. [Smart and Moore (2005), Giacovazzo (2002)] Crystalline materials with three-dimensional atom arrangements at a specific distance. Crystalline materials have distinctive planes that diffract X-rays in the form of unique intensity peaks. XRD peaks location and intensity depend on unit cell types and atomic position in unit cell. Miller indices are very useful for distinguishing unknown materials**.**

X-ray diffraction spectra of materials were reported using a MiniFlex600 (Rigaku, Tokyo, Japan) composed of four components i.e generator, goniometer, optics, and detector. 40kV tube voltage used towards metal target and corresponding tube current in the generator is 15mA. Optional graphite monochromator, soller slit (5.0° or 2.5°), and fixed dispersion slit are optics components. Vertical form goniometer with a 150 nm radius operating under ± 0.02°. NaI scintillator sensitivity and high speed silicone strip detector present in Miniflex600. Instrument use radiation Cu-Kα (ľ=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, RigakuMiniflex600 (Japan)

Incident X-ray interacts with material and corresponding diffraction observed by atomic plane. If the interplanar spacing (d) is an integer multiple of X-ray wavelength, the diffracted X-ray constructively interfere. The linear correlation between wavelength and interplanar spacing of solid powder material calculated by Bragg's 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.

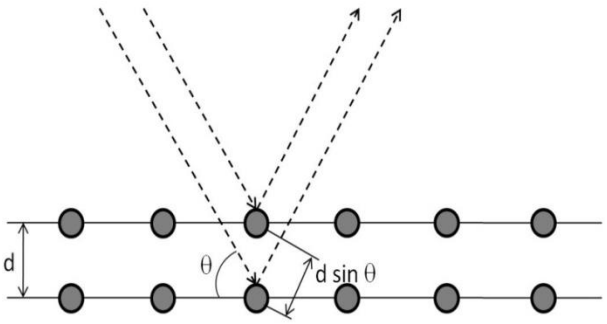

Figure 2.3. Braggs law of diffraction

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 commonly used to scan the surface of materials to investigate microscopic structure. This uses a focused beam of high-energy electrons to produce a spectrum of signals on the solid specimen surface. The signals deriving from electron-sample interactions reveal sample information including external morphology (texture), chemical composition, and crystalline structure and orientation of the sample materials. SEM was used to test the filler particle dispersion uniformity, agglomerate size and contact between the filler particles. Before observation the cross section of the sample was polished for SEM analysis. In the case of non-conductive dielectric content, to obtain good images, a thin layer of gold or silver was sputter-coated on the material surface.

The ceramic microstructure was determined using Scanning Electron Microscope (SEM) (JEOL JSM5410 model), one of the surfaces of the sintered pellets was polished successively using emery papers of various grades, 1/0, 2/0, 3/0, and 4/0. They were further painted using diamond paste on a velvet cloth. For broken as well as engraved surfaces SEM micrographs have been observed. For a few seconds HF acid was used on the pellet surface for etching.

Figure 2.4. Scanning Electron microscopy (SEM, ZEISS model, EVO18 Germany) and EDX Analysis instrument (Oxford instrument; USA)

2.5.4. Energy Dispersive X-ray Analysis (EDX)

Energy Dispersive X-Ray Spectroscopy is a technique of micro analytics that can be combined with Scanning Electron Microscopy (SEM). Combined with these imaging tools, EDX can provide elementary analysis on areas of diameter as small as nanometers. The electron beams effect on the sample creates X-rays indicative of the elements found in the sample. When the sample is bombarded by SEM electron beam, electrons are expelled from the atoms that form the surface of the sample. The resulting electron vacancies are filled in by higher-state electrons, and an X-ray is emitted to balance the energy difference between the states of the two electrons. 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 in which an ultra thin specimen is transmitted by a beam of electrons, communicating with the material as they pass through. The image is created by the interaction of the transmitted electrons through the specimen, which is magnified and projected on an imaging system 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. Using a sonicator, a pinch of fine ceramic powder was well dispersed in acetone and ethanol. A reduction of the solution was placed on a copper grid with carbon coating. Upon drying sample is ready through the microscope for TEM examination. TEM micrographs represent ceramic nanocrystalline character. The diffraction pattern was indexed based upon ceramics based on hexagonal perovskite.

Figure 2.5 Transmission electron microscope (TEM, FEI Tecnai-20G2)

2.5.6. Atomic force microscopy

The AFM has three major abilities: force measurement, imaging, and manipulation. In force measurement, the AFMs can be used as a function of their mutual separation to measure the force between the probe and the sample. this can be applied to perform force spectroscopy, to measure the samples mechanical properties, such as young's modulus, a stiffness measure. For imaging, the probe's reaction to the forces imposed on it by the sample can be used to form a high-resolution image of the three-dimensional shape (topography) of a sample surface. This is achieved by raster scanning the sample position with respect to the tip and recording the probe height corresponding to a constant probe-sample interaction (see AFM topographic image section for more details). The topography of the surface is commonly shown as pseudo-color plot.

The forces between tip and sample may also be used in manipulation to controllably change the properties of the sample. 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 [Mc El fresh (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.

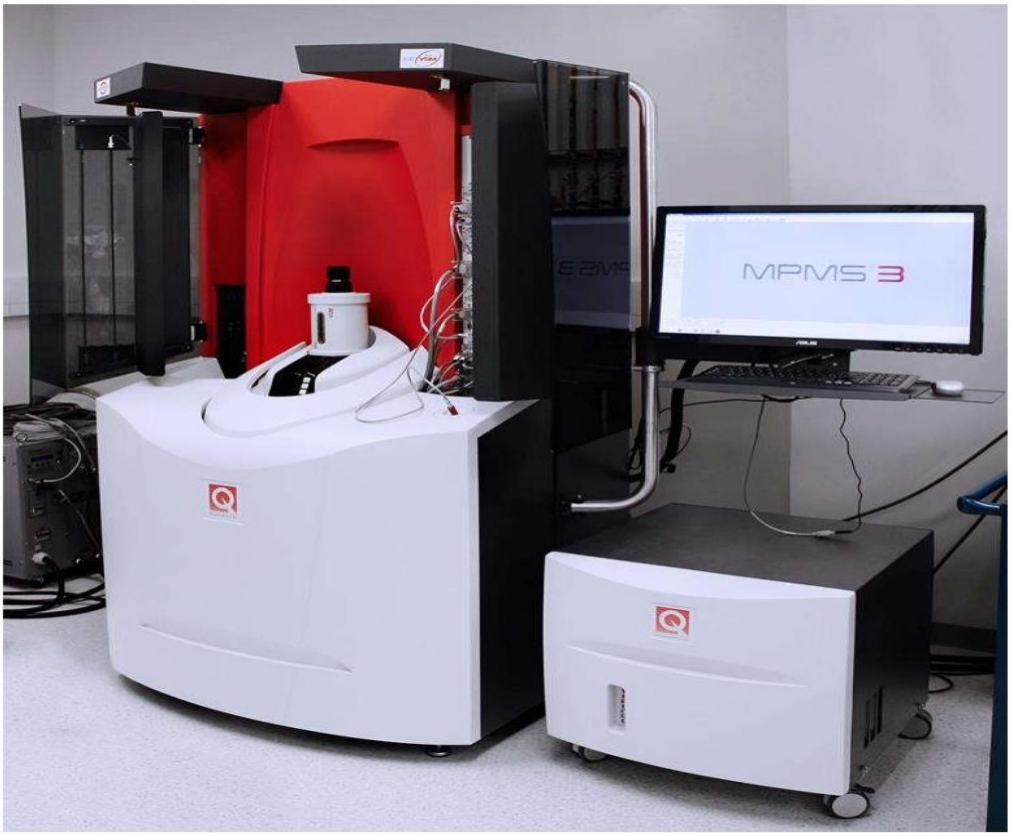

Figure 2.6 Superconducting quantum interference devices (SQUID) (Quantum Design, MPMS 3)

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 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 δ) can be calculated from the capacitance and conductance measured by equations:

$$C = \varepsilon_0 \varepsilon_r A / d \qquad (2.1)$$

$$\varepsilon = \frac{C \times d}{\varepsilon_0 A} \qquad (2.3)$$

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \qquad (2.4)$$

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**.**

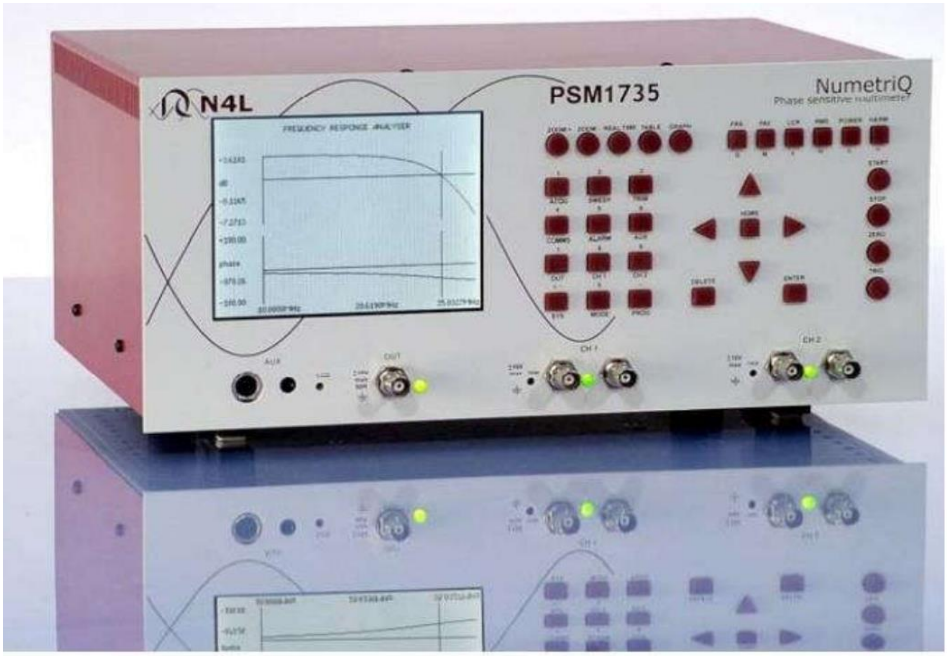

Figure 2.7 LCR Meter (PSM 1735, Newton 4th Ltd, U.K.) used for dielectric Measurement.

2.5.9. Impedance and Conductivity

The simple equivalent resistor–capacitor (RC) circuit and the modified constant phase element (CPE) circuit were used to define the impedance spectroscopy, and the CPE circuit obtained excellent agreement between the determined and measured curves. Through changing the annealing environment and temperature, the resistance and capacitance of the grain and grain boundaries may be controlled. The electrical resistance of the grain boundaries changed greatly under an oxygen absent annealing environment but the grain resistance showed almost no improvement. The reverse process occurred while under an atmosphere that anneals oxygen. Based on this finding, it is shown that the origin of the semi-conductivity of the grains in polycrystalline composite films derives from their oxygen loss, while the grain boundaries are similar to oxygen-stoichiometry.