
Chapter 2

*Materials synthesis
and characterizations*

2.1. Experimental procedure:

This chapter describes the details of experimental procedure for the synthesis of undoped and doped Bismuth Copper Titanium Oxides along with different physiochemical techniques used for their characterization. Materials research within the area of electronic ceramics involves (i) Synthesis of many compositions in the system of interest (ii) Crystal phase analysis, (iii) Microstructural analysis and (iv) dielectric performance of the synthesized ceramics. In the present study, different samples in the systems (a) $\text{Bi}_{2/3}\text{Cu}_{3-x}\text{Mg}_x\text{Ti}_4\text{O}_{12}$ (where $x= 0, 0.05, 0.1, 0.2$) (b) $\text{Bi}_{2/3}\text{Cu}_{3-x}\text{Ni}_x\text{Ti}_4\text{O}_{12}$ (where $x= 0.05, 0.1, 0.2$) (c) $\text{Bi}_{2/3}\text{Cu}_{3-x}\text{Zn}_x\text{Ti}_4\text{O}_{12}$ (where $x= 0, 0.05, 0.1, 0.2$) (d) $\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_{4-x}\text{Ge}_x\text{O}_{12}$ (where $x= 0.05$) and (e) $\text{Bi}_{2/3}\text{Cu}_{3-x}\text{Zn}_x\text{Ti}_{4-x}\text{Ge}_x\text{O}_{12}$ (where $x=0.05$) were produced by semi-wet route. All the samples were characterized for their crystal structure, microstructure, electrical and dielectric characteristics. For synthesis of various conformations in the above systems, we have used high purity raw materials such as Bismuth nitrate, Copper acetate, Titanium dioxide, Magnesium acetate, Zinc acetate, Nickel nitrate, Germanium Oxide and Citric acid with specifications given in Table 2.1

Table 2.1: Specification of the materials used for Synthesis

Raw materials	Minimum assay	Manufacturer
$\text{Bi}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$	99 %	Merck (India)
$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	98%	Merck (India)
$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	98.5%	Merck (India)
$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	98.5%	Merck (India)

Ni(NO ₃) ₂ .6H ₂ O	99%	Merck (India)
GeO ₂	99.99 %	Merck (India)
TiO ₂	98.5%	Merck (India)
Citric acid	99.5%	Merck (India)

2.2. Synthesis of materials:

a) Semi-wet route

The semi-wet route is adapted sol gel method. 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 oxidant present in the precursor solution. Citric acid used for a fuel while nitrates and acetates of diverse metals are used as an oxidant. Some chelating agent like EDTA, acetic acid, etc. can form 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) Preparation of ceramic material

In this route, nitrate solutions of each of Bismuth Bi(NO₃)₃.5H₂O, Copper acetate Cu(CH₃COO)₂.H₂O, Zn(CH₃COO)₂.H₂O, Mg(CH₃COO)₂.H₂O, Ni(NO₃)₂.6H₂O, TiO₂, and GeO₂ were taken in stoichiometric molar ratio. Solutions of these chemicals were prepared using distilled water and mixed in a beaker. 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 343-353 K to evaporate water. The residual mass was dried at 373-393 K in hot air oven. The ash was calcined at 1073 K 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 5 tons for 1 min.

The pellets were sintered at 1123 K for 8 h for dielectric measurements. A flow chart showing the various steps in the preparation of these materials by this method is shown in figure 2.1.

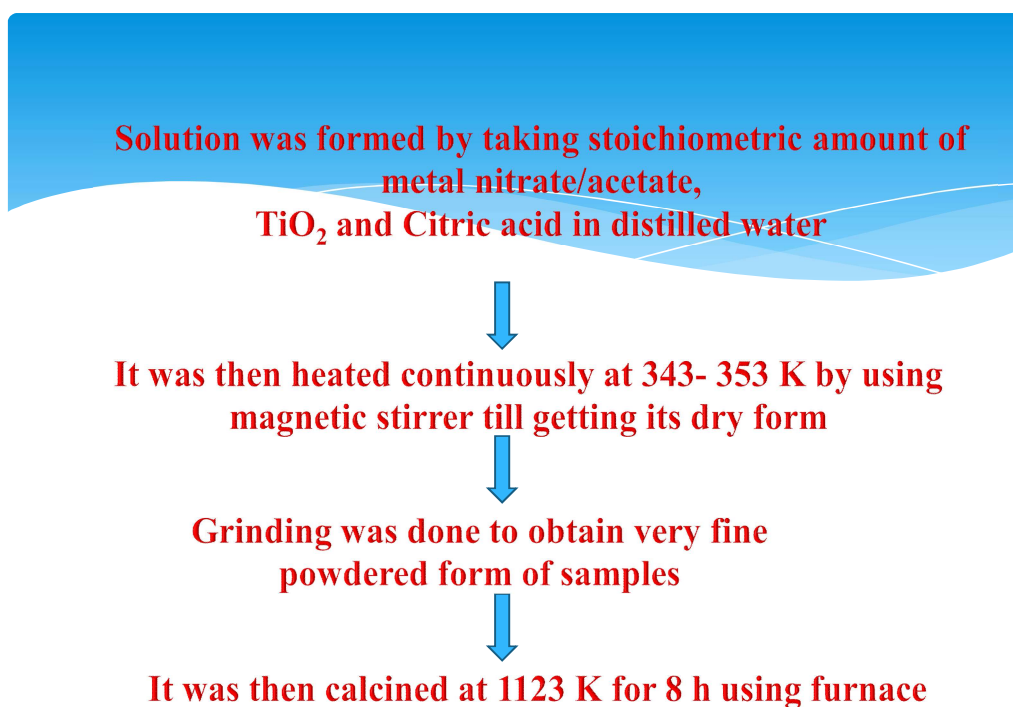


Fig. 2.1. Flow chart for the synthesis of complex perovskite by the semi-wet route.

2.3. Calcination process

- Calcination is a heat treatment process applied to solid materials to bring about a thermal decomposition, phase transition or deduction 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 partial 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 pellets (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.

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 from 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 pellets were ground and powder X-ray diffraction pattern were recorded using an X-ray diffractometer (Rigakuminiflex 600, Japan) with Cu-K_α radiation ($\lambda = 1.54 \text{ \AA}$) at scanning rate of 2°/min. The phase development 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 Hanawant'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 existing 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.2.2. Powder X-ray diffractometer, RigakuMiniflex600 (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.

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

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. 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.2.3. Transmission Electron Microscope (TEM, FEI TECANI G² 20 TWIN, USA) used to determine 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 G² 20 TWIN, USA) equipped with LaB₆ 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 from 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.

2.7. 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.2.4. 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 $1\mu\text{m}$ and $1/4\mu\text{m}$ followed by thermal etching. In some cases, microstructural studies are carried out for fractured surfaces of the sintered pellets.

2.8. 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).

2.9. 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 °C for 15 min. The capacitance (C), resistance (R), dielectric loss ($\tan \delta$) 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.

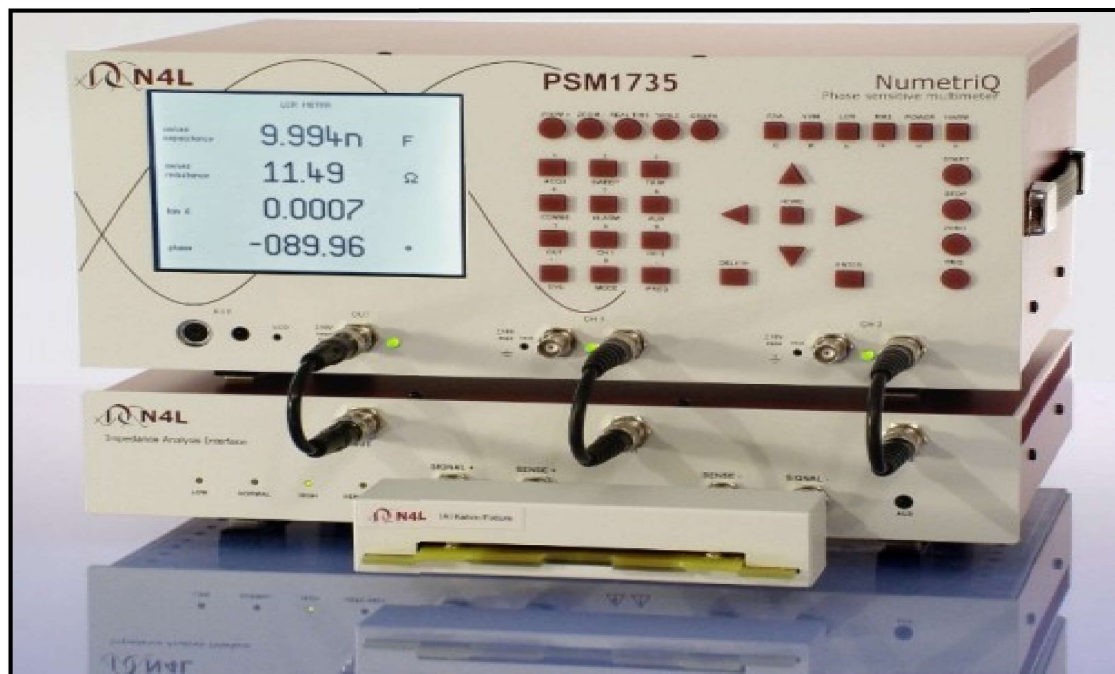


Fig.2.5. LCR meter (PSM 1735, Newton 4th Ltd, U.K.) used for dielectric properties measurement.

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

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

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.

2.10. Electrochemical characterization

cyclic voltammetry (CV), charge-discharge (CD), electrochemical impedance spectroscopy (EIS) of the three and two-electrode systems were performed by Versastat 3. In a three-electrode system, Ag/AgCl, Pt, and active material were taken as reference electrodes, counter electrodes, and working electrodes respectively. The mass loading of the working electrode was 2 mg/cm^2 . For Electrochemical Impedance Spectroscopy (EIS), 10 mV amplitude of AC voltage was applied over 100 kHz – 0.01 Hz frequency. For all the Electrochemical analyses, 1M KOH electrolyte was taken. Copper wire was taken as the current collector and a substrate (carbon paper) was attached to the copper wire with the help of conductive silver glue. The backside of the carbon paper and the exposed part of the copper wire was insulated by using gluestick. Then a dispersion was prepared to have 5 mg of prepared material, 2-propanol of 0.2 mL, Nafion of 12 μL , and drop cast on the carbon paper of 1 cm^2 area. The active mass loading was 2 mg/cm^2 . The scan rate was 5 mV/s. Then the prepared electrode was dried for around half an hour in a vacuum oven till the complete disappearance of the used solvents.