2.1. Experimental

This chapter explains experimental procedure for the synthesis of hexagonal perovskite as well as doping of iso-valent and hetero-valent metal ions in parent compound. 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 properties also investigated at some selected temperature and frequencies. In the present investigation, various samples in different systems were synthesized viz. (i) $Ba_4YMn_3O_{11.5-\delta}$ (BYMO) (ii) $Ba_4YMn_{3-x}Fe_xO_{11.5}$ (x= 0.05, 0.1 and 0.2) synthesized by chemical route (iii) $Ba_6Y_2Ti_4O_{15}$ (BYTO) (iv) $Ba_6Y_2Ti_{4-x}Fe_xO_{15}$ (x = 0.05, 0.1 and 0.2) synthesized by semi-wet route. All samples were characterized by various techniques like Thermos-gravimatric/Differential thermal analysis (TG/DTA), 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 and PE loop tester respectively at the temperature range of 300- 500 K, 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. Materials used

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

2.2.1. Chemicals

Barium nitrate, Yttrium nitrate, Manganese nitrate/acetate, Titanium oxide, Iron nitrate and glycine with specification are given bellow in Table 2.1.

Table 2.1 Specification of the chemicals used are as follows

Raw Materials	Minimum Assay	Manufacturer
$Ba(NO_3)_2$	99 %	Merk
$Y(NO_3)_3.6H_2O$	99.8 %	Sigma-Aldrich
$(CH_3COO)_2Mn.4H_2O$	99.99 %	Sigma-Aldrich
$Fe(NO_3)_2.9H_2O$	98 %	Merk
TiO_2	99 %	Merck
Glycine	99 %	Merck

2.3. Preparation of materials

2.3.1. Preparation of metal nitrate solutions

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

2.4. Synthesis method

The synthesis of un doped and doped BYMO by chemical route i.e. glycine assisted sol gel route, whereas iron and niobium doped BYTO and un doped BYTO synthesized by semi wet route.

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 a 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 ^{0}C 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. Schematic diagram for the synthesis of ceramics is shown in Figure 2.1.

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 ^{0}C for 5 h and further 800 ^{0}C for 8 h 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.
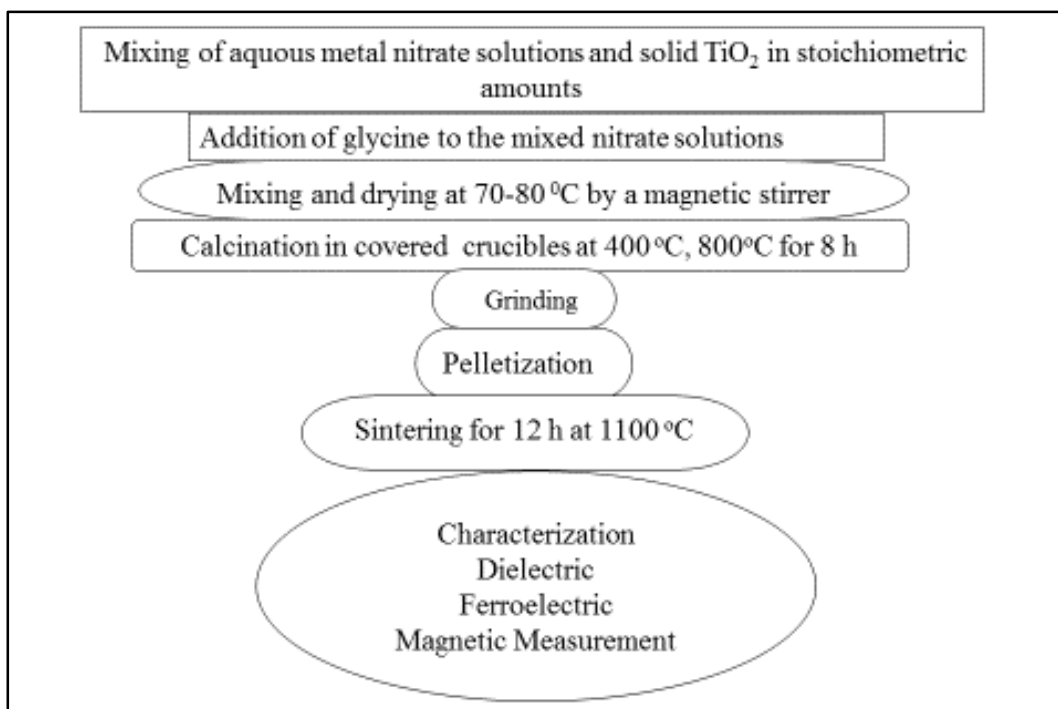
Figure 2.1 A flow chart indicating the various steps for the preparation of materials

This ash was calcined in air at 800 ^{0}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 ^{0}C for 12 h for dielectric and ferroelectric measurements.

2.5. Characterization techniques for synthesized ceramic materials

2.5.1. Thermal Analysis: Thermo-Gravimetric and Differential Thermal Analysis

The thermo-gravimetric (TG) and differential thermal analysis (DTA) are the techniques which measure a change in a material as a function of temperature. It is useful in characterizing decomposition and crystallization during ceramic powder processing and in determining an

optimum calcination temperature. In TG/DTA techniques a precursor powder specimen and an inert reference material are heated concurrently at a linear rate each having its temperature sensing and recording apparatus. The thermal energy changes, either endothermic or exothermic which occur in the course of heating are plotted. These plots provide data on the chemical and physical transformations such as melting, sublimation, glass transitions, crystal transitions and crystallization. A thermos-gravimetric analyzer (Pyris Diamond TG/DTA, Perkin-Elmer Instrument, USA) is used to characterize the material mass change either as a function of temperature or isothermally as a function of time in a controlled atmosphere. It can be used to characterize a material that exhibits a weight change due to decomposition, oxidation or dehydration. In this analysis about 20 mg dry precursor powder of materials were placed in the sample holder and then heated from room temperature to 1000 ^{0}C with heating rate of 10 ^{0}C /minute in nitrogen atmosphere. TG curve shows the variation of mass of the material as a function of temperature. In DTA, the samples under study and an inert reference are made to undergo identical thermal cycles while recording any temperature difference between sample and reference. This differential temperature is then plotted against time or against temperature to get DTA curve or thermogram. The change in the sample, either exothermic or endothermic, can be detected about the inert reference. Through this analysis, energy required for a particular type of phase transformation in the material can be determined. DTA curve provides data on the transformations that have occurred, such as phase transitions, crystallization, melting and sublimation.

2.5.2 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 arrangements 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 are very useful for characterizing unknown materials. X-ray diffraction spectra of materials were recorded using a MiniFlex 600 (Rigaku, Tokyo, Japan) (Figure 2.2) the instrument consist of four components i.e., generator, optics, goniometer and detector. In generator, 40 kV tube voltage used towards metal target and corresponding tube current is 15 mA. 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 150 nm working under accuracy of ± 0.02 ° is maintained. NaI scintillator and high speed silicon strip detector present in Miniflex 600. Instrument employing Cu-K$_\alpha$ 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 Miniflex 600 (Japan)

Incident X-ray interacts with material and corresponding diffraction observed by atomic plane. If the inter planar spacing (d) is an integer multiple of X-ray wavelength, the diffracted X-ray constructively interfere. The linear correlation between wavelength and inter planar spacing of solid powder material calculated by Bragg's equation written as equation (2.1)

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

Where n is order of reflection i.e. 1, 2, 3, λ represents wavelength of incident radiation, d is the inter planar spacing and θ is Bragg angle. The Braggs diffraction was given in Figure 2.3.
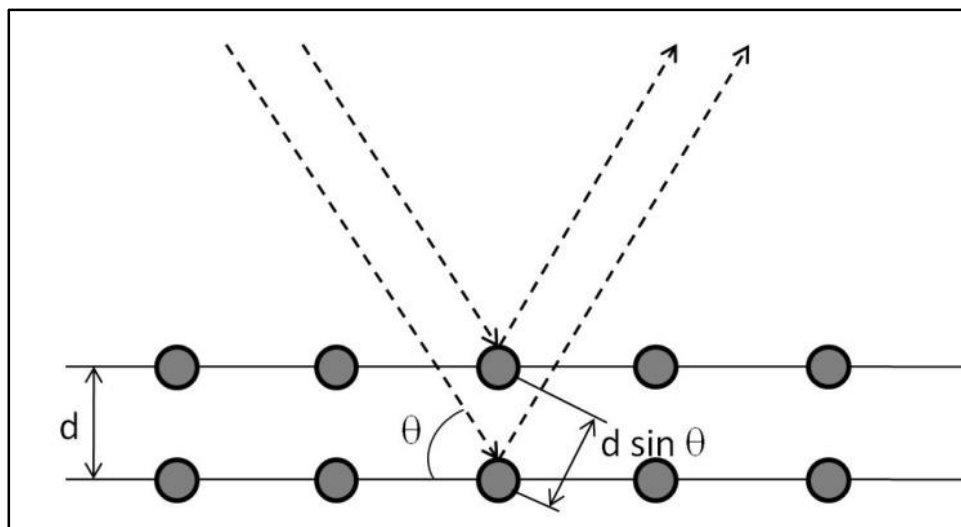
Figure 2.3 Braggs law of diffraction

The average crystallite size was calculated by Scherrer formula as given bellow in equation (2.2).

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

Where D is the crystallite size (in nm), k represents dimensionless constant ($\approx$ 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-20 G^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, the 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. 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.

2.5.7. Automatic PE loop tracer

It is designed for characterization of materials such as ferroelectrics. For ferroelectrics materials polarization is plotted against the electric field. The measurement is performed at line different frequencies of 50 Hz to 1 kHz. The complete measurement system consists of PE main unit, sample holder and furnace with temperature controller. PE test system based on sawyer tower circuit in which two capacitors are connected in series and AC voltage is applied on both the series so that charge on both capacitors will be the same. In order to get complete saturation, the internal capacitance must be greater than the sample capacitance.

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 ^{0}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 (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:

$$C = \varepsilon_0 \, \varepsilon_r \, A \, / \, d \qquad\qquad (2.3)$$

$$\varepsilon = \frac{C \times d}{\varepsilon_0 A} \qquad\qquad (2.4)$$

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \qquad\qquad (2.5)$$

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.