
Chapter 2

Experimental Procedure for the synthesis & characterization

Experimental Procedures for the synthesis and characterization

2.1. Materials Design and methods for the synthesis and characterization

Experimental procedure for the synthesis of M-type hexagonal barium hexaferrite ceramic materials describes in this chapter. Ceramic materials are hard, heat-resistant and corrosion-resistant, and brittle in nature and also have very interesting properties. Their properties were improved by different synthetic routes. Single phase formation of these materials was controlled by reaction atmosphere, reaction time and sintering temperature. Different types of physiochemical techniques were carried out for their characterization to observe information about microstructure and particle size of synthesized materials. Dielectric and magnetic properties were also investigated at few selected temperature and frequency. In the present investigation, various samples in different systems were synthesized by chemical route

(i) $\text{BaFe}_{12}\text{O}_{19}$ (BHF) by Chemical route

(ii) $\text{BaFe}_{12-x}\text{Co}_x\text{O}_{19}$ ($x=0.0, 0.05, 0.1$) by chemical route

(iii) $\text{BaFe}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x=0.0, 0.05, 0.1$) by chemical route and its composite with $\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (BCTO) was also synthesized by chemical route

Characterization of all synthesized materials were carried out by different techniques such as Powder X-ray diffraction, Fourier transmission electron spectroscopy (FTIR), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX) and Atomic force microscopy (AFM). Dielectric and ferroelectric properties of all the materials were measured with the help of LCR meter, respectively within the temperature range (300- 500 K) and few selected frequencies. Magnetization versus magnetic field (M-H) hysteresis of the all materials was measured by MPMS (SQUID magnetometer

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quantum design) at few selected temperature whereas magnetization with temperature (M-T) recorded in the temperature range of 5 – 300K.

2.2. Material used

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

2.2.1 Chemicals

Barium nitrate, Iron nitrate, Cobalt nitrate, Nickel nitrate, 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
Ba(NO ₃) ₂	99 %	Merck
Fe (NO ₃) ₃ .9H ₂ O	99.8%	Merck
Co (NO ₃) ₂ .6H ₂ O	99.5%	Merck
Ni(NO ₃) ₂	99.8%	Merck
citric acid	99.5%	Merck

2.3. Preparation of materials

The synthesis of materials involves following steps

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2.3.1. Preparation of metal nitrate solution: All the metal nitrates of Ba, Fe, Co, and Ni were taken as in their stoichiometric amount that mentioned in the table and dissolved in the double distilled water to form homogeneous solutions if required, the solution was heated on a hot plate.

2.4. Synthesis methods: The undoped $\text{BaFe}_{12}\text{O}_{19}$ (BHF), cobalt (Co), $\text{BaFe}_{12-x}\text{Co}_x\text{O}_{19}$ ($x = 0.0, 0.05, 0.1, 0.2$) and nickel (Ni), $\text{BaFe}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0.0, 0.05, 0.1, 0.2$) doped barium hexaferrite ceramic were successfully synthesized by chemical route.

2.4.1. Chemical route

This method is a type of combustion synthesis technique by use of citrate/glycine-nitrate as a complexing agent. This synthesis technique is generally useful for obtaining multicomponent single phase of the materials which 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 calcinations of the ash at high temperature. In Chemical route developed by us, all the metal cations were taken as nitrate and Citric acid/Glycine was used as the fuel. Stoichiometric amounts of metal nitrate were dissolved in double distilled water and aqueous solution of citric acid per equivalent to metal ions was added to the solutions. The resulting solutions were then heated on a hot plate with magnetic stirrer at $70-80^\circ\text{C}$ 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

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and obtained ignition product ash was porous in nature. The obtained precursor dry powder is calcined at a particular temperature for a certain period of time. Then, the calcined powder is ground again with the help of mortar and pestle and converted in to fine powder. An appropriate amount of polyvinyl alcohol (PVA) act as suitable binder is added to the powder and mixed uniformly and then it is pressed in to a suitable shape.

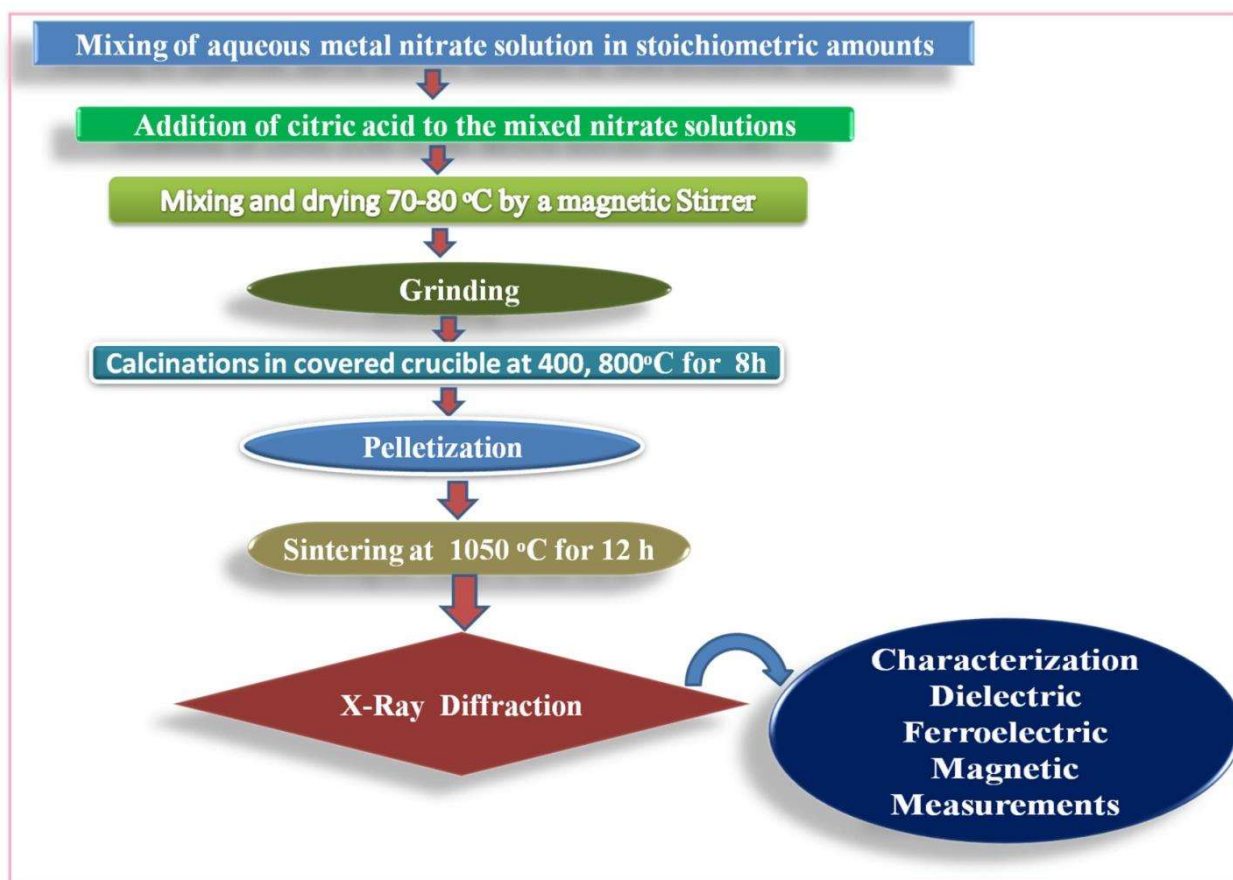


Figure 2.1.Flow chart for the synthesis of materials by chemical route.

The resulting product is first heated slowly to a particular temperature to remove the binder and then the temperature of the sample is increased to a particular value and maintained at this value for certain duration for annealing. After annealing, the sample is cooled under

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controlled rate of cooling. The final resulting product is achieved by diffusion of metal ions at high temperature. A systematic flow chart of synthesis procedure is shown in Figure 2.1

2.4.2. Calcination Process

This process is applicable for phase transition, thermal decomposition, or removal of a volatile fraction of solid powder materials by heat treatment. Calcinations process was carried out in the absence or limited supply of air or oxygen below its melting temperature. The synthesized materials were calcined at 800 °C for 8 hrs in a Muffle furnace.

2.4.3 Sintering Process

This process is useful for densification of a porous compact and done by heating the materials at the certain temperature. Mostly cylindrical pellets were prepared with the help of hydraulic press on applying pressure 4- 5 tones and further, these pellets were sintered for phase confirmation of the compounds. For this, the obtained dry precursor firstly calcined in air at 800°C for 8 h in a muffle furnace and then the resultant mixer were ground with the help of a pestle and mortar into fine powder. Few drops of 2%PVA as a binder were mixed in to the fine calcined powder and made the cylindrical pellets by using a hydraulic press. Further, the cylindrical pellets were heated at 500 °C for 3h for removing the binder and then sintered at 1050°C for 12h for dielectric, magnetic 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 rapid analytical technique that is useful for the crystalline phase identification and orientation and also useful for determination of structural properties such as Lattice parameters, grain size, epitaxy, phase composition, strain, and thermal expansion of all

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types of materials, crystals and powders [Smart and moore (2005), Giacovazzo (2002)]. As all the physical properties of the solids like electrical, magnetic, ferroelectric as well as optical is part of characterization that depends upon the arrangement of the atoms in 3 D space. 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.



Figure 2.2. Powder XRD instrument, RigakuMiniflex600 (Japan)

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X-ray diffraction spectra of materials were recorded using a MiniFlex600 (Rigaku, Tokyo, Japan). These instrument containing four components such as 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 mm is working under accuracy of $\pm 0.02^\circ$. NaI scintillator and high speed silicon strip detector present in Miniflex600. The XRD diffraction patterns recorded at scan rate of $1^\circ/\text{min}$ keeping step size of 0.02 and employing $\text{Cu-K}\alpha$ radiation ($\lambda=1.54059 \text{ \AA}$).

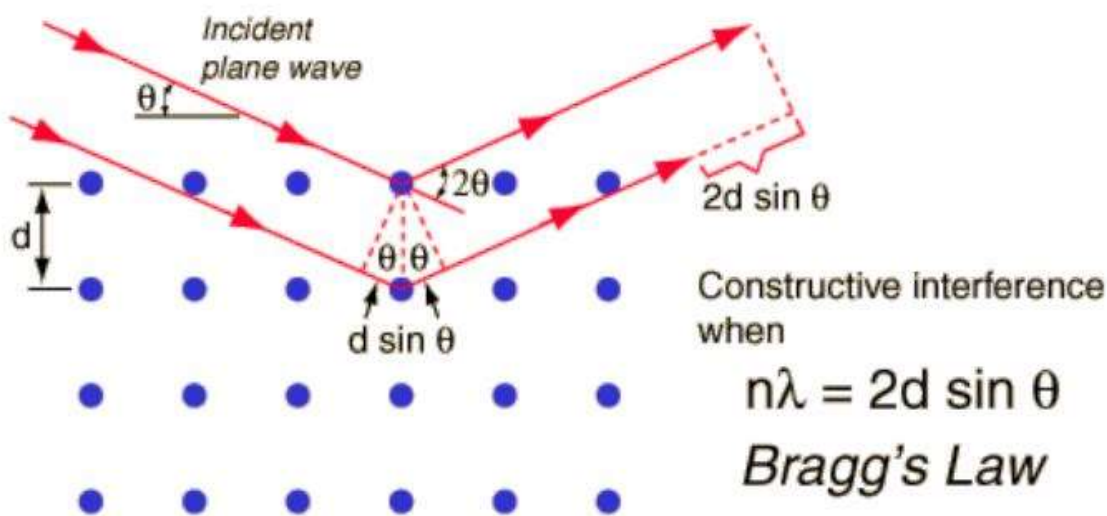


Figure 2.3. Braggs law of diffraction

This technique is based on constructive interference of monochromatic X-rays radiation with crystalline materials in which the X-rays produced from a cathode ray deperate produced a monochromatic radiation which are directed towards the sample. When the incident X-ray or

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other electromagnetic waves interacts with the electron clouds of the atoms within the materials, they are scattered by the adjacent atoms in the crystal due to shorter wavelength which interferes constructively and produced diffraction by atomic planes. If the diffracted ray produced a constructive interference, the relation between wavelength (λ) and inter-planar d-spacing (d) of solid powder is calculated by using Bragg's Law.

$$2d \sin \theta = n \lambda \quad (2.1)$$

Where n is order of reflection i.e 1, 2, 3, λ represents wavelength of incident radiation, d is the inter-planer spacing and θ is Bragg angle.

The size of micrometer particles or crystallite in the solid was calculated by Scherer formula as given bellow

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

where, D is the crystallite size (in nm), k is the dimensionless shape factor with value close to unity (≈ 0.9), λ is wavelength of X-ray radiation, β is the full width at half maximum intensity (FWHM) measures line broadening and their values were taken as in radian and θ is Bragg's diffraction angles.

2.5.2. Scanning Electron Microscopy (SEM) Analysis

The Scanning Electron Microscopy is the type of electron microscope that has been widely used in modern material science research areas. They produced an image of the sample by scanning the surface with focused beam of electrons in three dimensional appearances. It uses a focused beam of high-energy electrons at the surface of solid specimens to generate a various signals that give the information about the surface topography with clarity and elemental compositions of the

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materials. The position of electron beam that is scanned in the raster scan pattern is interacting with the detected signal to produce an image of the materials. The fundamental units of SEM are electron-optical columns together with appropriate electronics, the vacuum system, which includes the specimen chamber and stage and signal detection and display systems. 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 topographical studies of the materials by the SEM instrument, make a cylindrical pellets which is non-conducting in nature with appropriate thickness and diameter were polished by using emery papers of different grades, 1/0, 2/0, 3/0, and 4/0 consecutively to becomes smooth surface and then coated with the conducting materials such as gold, silver, osmium, gold/palladium alloy, iridium, chromium, tungsten, platinum and graphite on the surface of this pellets for obtaining good quality of the image by using a vacuum coating unit. The microstructure of ceramics was determined using Scanning Electron Microscope (SEM) (Model JEOL JSM5410) at 20 kV. SEM images of the samples 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. Grain size of the samples was calculated by taking more than 100 grains with the help of Image J software at the different regions of each sample and taking their root mean square diameter.



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

2.5.3. Energy Dispersive X-ray Spectroscopy (EDX)

Energy Dispersive X-Ray Spectroscopy sometimes also called as energy dispersive X-ray analysis (EDXA) or Energy Dispersive X-Ray microanalysis (EDMXA) is a micro analytical technique that can be attached with Scanning Electron Microscopy (SEM). EDX combined with these imaging tools can give the information 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

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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 materials are investigated by EDX (Model JEOL JSM5410).

2.5.4. Transmission Electron Microscopy (TEM) Analysis

Transmission electron microscopy (TEM) is a microscopic technique where by a beam of electrons are 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. Transmission electron microscopes are able to take images at extensively higher resolution due to smaller de Broglie wavelength in comparison to that of light microscopes, This facilitate the instrument to capture single atoms that are thousands time smaller than observable object seen by a light microscope. It is a major analytical method in the field of chemical, physical, and biological sciences. It has useful many applications such as virology, material science, cancer research and pollution, nanotechnology and semiconductor research and also may be useful in other fields such as palynology and paleontology. Bright field TEM images and selected area diffraction patterns (SAED) were obtained by transmission electron microscope (TEM, FEI Tecnai-20G²) equipped with LaB₆ filament with an accelerating voltage of 200 kV.

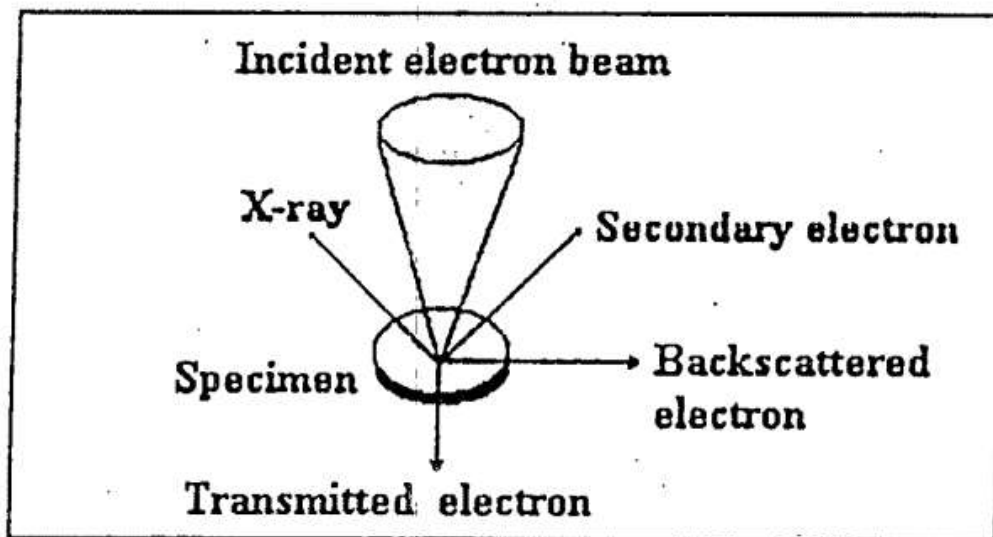


Figure 2.5(a). Signal produced near the surface of specimen due to interaction with electron beam.

For TEM measurement, a pinch of fine ceramic powder was dispersed well in ethanol using a sonicator. A drop of this solution was put on a carbon-coated copper grid and kept in the oven up to 24 h for drying sample after which ready dry sample for TEM analysis through the microscope. TEM micrographs depict nanocrystalline nature of the ceramic. The diffraction pattern observed in SAED pattern and HR-TEM image has been indexed on the basis of hexagonal perovskite based ceramics.



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

2.5.5. Atomic force microscopy

Atomic force microscopy (AFM) is a very-high-resolution type of scanning probe microscopy (SPM) which signifies resolution on the order of fractions of a nanometer and having more than 1000 times better resolution than the optical diffraction limit. Tapping mode Atomic Force Microscope (Bruker, Dimension Edge with Scan Asyst) was used for measurement of particle size distribution and average roughness. The AFM has three major abilities: force measurement, imaging, and manipulation.

In force measurement, AFMs can be used to measure the forces between the probe and the sample as a function of their mutual separation. This can be applied to perform force spectroscopy, to measure the mechanical properties of the sample, such as the sample's Young's

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modulus, a measure of stiffness. For imaging, the reaction of the probe to the forces that the sample imposes on it can be used to form an image of the three-dimensional shape (topography) of a sample surface at a high resolution. This is achieved by raster scanning the position of the sample with respect to the tip and recording the height of the probe that corresponds to a constant probe-sample interaction (see section topographic imaging in AFM for more details). The surface topography is commonly displayed as a pseudo colour plot.

In manipulation, the forces between tip and sample can also be used to change the properties of the sample in a controlled way. Examples of this include atomic manipulation, scanning probe lithography and local stimulation of cells.

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.



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

2.5.7. Electric and Dielectric Measurement:

The cylindrical pellets were polished with emery paper (ranges from 0 to 6) to make a flat surface and pasted with silver paint on the both side of flat surfaces which was dry over at 150 °C for 10 min for dielectric and electric measurement of the ceramic materials. The capacitance (C), resistance (R) and dielectric loss ($\tan \delta$) of the cylindrical pellet of the ceramic was calculated by the LCR Meter (PSM 1735, Newton 4th Ltd, U.K.) as function of temperature 300-500 K in the frequency range (100 Hz to 20 MHz) with a bias voltage of 1 Volt. The dielectric constant (ϵ) and dielectric loss values of the materials were calculated by taking capacitance data. The

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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 find the values of resistance and capacitance of the material which is due to separate contributions of grains, grain boundaries and electrode polarization effect.

2.5.8. Impedance and Conductivity

The simple resistor–capacitor (RC) equivalent circuit and the modified constant phase element (CPE) circuit were used to describe the impedance spectroscopy, and excellent agreement between the calculated and measured curves was obtained in the CPE circuit. The resistance and capacitance of the grains and grain boundaries can be tuned by changing the annealing atmosphere and temperature. Under oxygen absent annealing atmosphere, the electric resistances of the grain boundaries changed greatly but the resistance of the grains showed almost no change. While under an oxygen annealing atmosphere, the reverse process occurred. On the basis of this result, it is demonstrated that the origin of the semi conductivity of the grains in composite polycrystalline films arises from their oxygen-loss, while the grain boundaries are close to oxygen-stoichiometry.

2.5.9. Automatic PE loop tracer

It is designed for characterization of materials such as ferroelectrics. The plots of polarizations versus electric field were taken for ferroelectric measurement of the materials. The measurements were taken at the different frequencies from 50 Hz to 1 kHz. The complete measurement system consists of PE main unit, furnace with temperature controller as well as sample holder. PE test system based on sawyer tower circuit in which two capacitors are connected in series and AC voltage applied on both the series so that charge on both capacitors

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will be the same. In order to get complete saturation, the internal capacitance must be greater than the sample capacitance.