CHAPTER-3
SYNTHESIS AND CHARACTERIZATION TECHNIQUES

3.1 Introduction

There are various techniques such as conventional solid-state reaction, sol-gel, auto-combustion, green nano-technology, reactive milling egg-white precursor and co-precipitation technique for the synthesis of bulk and nano materials for achieving fine particle size, homogeneity and high purity [96, 97]. Among these the sol-gel and microwave heating synthesis technique is adopted in the present work owing to rapid heating and low cost of sample preparation. Further the samples are characterized using X-ray diffractometer (Bruker, X-ray powder diffractometer, CuKα, λ = 0.15418 nm) at room temperature for structural identification. Field Emission Scanning Electron Microscope (FESEM: Hitachi S-4700) and High Resolution Transmission Electron Microscope (HRTEM: Model Tecnai G20, FEI, USA) are used for the study of surface morphology and the optical properties are carried out by UV-Visible spectrophotometer (JASCO V-670 PC) and FTIR. To study the elemental and electrical properties LCR HiTESTER (HIOKI 3532-50, Japan) is used. The pellets sputtered with silver paste are used for the measurement of electrical properties. ac electrical properties are carried out by placing the pellets in a programmable furnace interfaced to LCR bridge and a PC in the temperature range of 30-600°C at operating frequencies from 42 Hz - 5 MHz. In order to study the conduction mechanism among all samples, the ac-conductivity (σac) analysis has been carried out. Further, the dielectric properties like dielectric constant (ε') and dielectric loss tangent (tan δ) are studied. P-E loop tracer (Marine India Ltd.) is used to study the ferroelectric properties.

3.2 Synthesis Techniques

3.2.1 Sol-Gel Synthesis and Microwave Heated

The sol-gel technique is very popular wet-chemical method broadly used in the preparation of inorganic materials, normally metal oxides which are in nano dimension. This process was first demonstrated in 19th century, but it was practically proved by Steven S. Kistler in the year 1931. This method includes the evaluation of
inorganic systems (metal oxides) through the formation of sol (colloidal solution or precursor) and gelation of the sol to form a system in a continuous liquid phase (gel).

**Fig. 3.1 Sol-Gel Process of Nanomaterial Synthesis**

Initially the samples are processed to make a dispersible oxide and forms a sol (precursor) in contact with dilute acid or water, exclusion of the liquid from the sol (precursor) yields the gel, and the solution or gelation transition controls the shape and size of the particle. Calcination of the gel induces the oxide. The main advantage of this technique is the capability to regulate the microstructure of final outcome by controlling chemical reaction. It has been revealed that, modification of the reaction conditions may considerably have an effect on the structure of the sol–gel product. This method is extensively used in the fabrication of inorganic and organic-inorganic hybrid materials and has an ability of producing nanorods, nanoparticles, monoliths and thin films. As a whole, microwave technique is a rapid heating method in which the material absorbs microwave energy and is converted into heat energy within the sample volume. Therefore, very short period of time is consumed for heating the sample. Microwaves can be used to carry out selective heating, which is not possible by using conventional heat treatments. Microwave heating produces potentially a cleaner, faster, and cheaper heating aid. It’s been used in the food industry for
decades. In recent years, this method has been used in scientific laboratories for accelerating organic reactions.

3.2.2 Flow Chart for Synthesis of Lead Based Ceramics

![Flow Chart](image)

**Fig. 3.2 Synthesis of PbTiO$_3$ Nanoparticles**

3.2.3 Sample Preparation

At the outset, the initial materials were taken according to their stoichiometric ratio and weighed on a sensitive digital weighing balance. The precursor materials were lead acetate (Pb (CH$_3$COO)$_2$), cobalt nitrate (Co (NO$_3$)$_2$.6H$_2$O), lanthanum nitrate (La (NO$_3$)$_3$.6H$_2$O) and titanium butoxide (Ti(OC$_4$H$_9$)$_4$). All these compounds were selected corresponding to the stoichiometric ratio and glacial acetic acid (CH$_3$COOH) was taken as the solvent. The CH$_3$COOH solution was poured into a container and placed on the magnetic stirrer for persistently mixing the content. Later, Pb(CH$_3$COO)$_2$ was added and dissolved. After it was completely dissolved,
Co(NO$_3$)$_2$.6H$_2$O and La(NO$_3$)$_3$.6H$_2$O were added. The temperature was maintained at 50°C during the whole process. After half an hour, with the help of dropper Ti(OC$_4$H$_9$)$_4$ was added persistently drop by drop. The entire solution was allowed to mix carefully for two hours and solution of ethanol and water was added to the solution by using a burette. After some time, a gel like solution was attained. This gel was drained naturally for forty-eight hours, after that with the help if hot air oven for about one hour. Through this process a rigid crystal form was acquired which was grinded into a fine powder. Then the attained powder was sintered at 750°C by a microwave furnace for 45 minutes. Further the crystalline powder was grinded again to get fine powder. The pellets with a diameter of 12 mm and thickness of 2.2 mm were prepared by maintaining pressure of around 10 torr in the hydraulic press. In addition, the prepared samples were characterized using several characterization techniques like X-ray Diffraction, FESEM and High-Resolution Transmission Electron Microscope for structural and morphological analysis. Optical, ferroelectric and dielectric properties were studied using UV-Visible spectrophotometer, FTIR, P-E loop tracer and LCR Hi-TESTER.

3.3 Characterization Techniques

3.3.1 X-Ray Diffraction

X-ray diffraction analysis was carried out to characterize the crystalline nature and the structure of the prepared samples. The XRD spectrum was recorded on Bruker-D8, X-ray diffractometer using CuK$_\alpha$ radiation of wavelength 1.542 Å. The schematic diagram and photograph of X-ray diffractometer was shown in Figs. 3.3 and 3.4 respectively. The X-ray was scanned over the titanate samples in the range 20 =10-90° with scan rate of 0.02°. The X-ray generator was operated at 20 x 10$^{-3}$ A and 40 x 10$^{3}$ V. In a polycrystalline titanate powder, the tiny crystallites were oriented randomly. If the powder was struck by X-ray beam many planes would be oriented that ‘Bragg’s law’ was satisfied and XRD pattern was achieved. When a collimated beam of X-rays, with the wavelength range of 0.5 to 2 Å is incident on the powder, the X-rays diffracted by the crystalline phases from the specimen obeys the ‘Bragg’s law’ of diffraction (nλ = 2d sinθ, where ‘d’ is the inter-planar spacing and ‘n’ is the order of diffraction). The intensity of the diffracted X-rays was measured in terms of
the diffraction angle $2\theta$ and the specimen's orientation. The diffracted beam was collected by a detector and the outcome of detector was processed and then collected by an automatic recorder. The output was in the form of a chart which gives a record of intensity versus diffraction angle $2\theta$. The obtained diffraction pattern was used to detect the crystalline phases in the specimen in analyzing the sample(s) structural properties [98, 99]. The XRD gives information not only about the crystalline structure but also the crystallite size, lattice parameter and strain of prepared titanate samples.

Fig.3.3 Schematic Diagram of X-ray Diffractometer

Fig.3.4 Photograph of X-ray Diffractometer
The lattice parameter ‘a’, crystallite size ‘D_p’, theoretical density ‘ρ_x’, porosity ‘P’, dislocation density ‘ρ_d’ and strain ‘ε’ has been calculated from the XRD results using the expressions given below (Naidu et al., 2016 a).

\[ a = d \left( h^2 + k^2 + l^2 \right)^{1/2} \]  \hspace{1cm} (3.1)  
\[ D_p = \frac{0.9 \lambda}{\beta \cos \theta} \]  \hspace{1cm} (3.4)  
\[ \rho_x = \frac{8M}{N \cdot \alpha^3} \]  \hspace{1cm} (3.2)  
\[ P = 1 - \left( \frac{\rho_b}{\rho_x} \right) \]  \hspace{1cm} (3.5)  
\[ \rho_d = (D_p)^2 \]  \hspace{1cm} (3.3)  
\[ \varepsilon = \frac{\beta}{4 \tan \theta} \]  \hspace{1cm} (3.6)  

where 

- \( d \) = interplanar spacing,  
- \( (hkl) \) = miller indices  
- \( \lambda \) = wavelength  
- \( \beta \) = Full width half maxima  
- \( \theta \) = diffraction angle  
- \( M \) = molecular weight of the sample  
- \( N \) = Avogadro number  
- \( \rho_b \) = bulk density

### 3.3.2 Scanning Electron Microscopy (SEM)

SEM is an effective tool used to investigate surface morphology of solids [100] and is shown in Fig 2.4.3. The microstructures of the prepared samples were studied in the present investigation employing Hitachi S-4700 and Ultra 55 SEM Carl Zeiss electron microscopes in the scanning mode. The surfaces of the specimen were coated with the Gold (Au) film of 50Å thickness by sputtering technique. The Gold coated samples were kept on the sample holder of SEM, to make the sample conducting silver dag was used which was in contact with the sample holders metal base. Silver (Ag) paste affords a good electric contact and also works as a better adhesive, thus the sample cannot move while the sample holder was rotated. Back scattered and secondary emission electrons were used to give the image of the samples. Accelerating voltage of 25 x 10^3 volts and working distance of 6-15 mm has been maintained for all the samples and other details were given in the individual micrographs separately.
(including the selected area range in terms of micron to nano range). Average grain size (G	extsubscript{a}) is calculated using the linear intercept method (Naidu et al., 2016c).

\[ G_a = \frac{L}{MN} \]  

(3.7)

Where  
\( L = \) total test line length,
\( M = \) magnification and
\( N = \) total number of intercepts which the grain boundary makes with the line.

![Fig.3.5 Photograph of Scanning Electron Microscope (SEM)](image)

### 3.3.3 Transmission Electron Microscope (TEM)

Transmission Electron Microscope was shown in Figure. 3.6. HRTEM is an advanced microscopy technique based on wavelength constraint. In this a fine beam of electrons is transmitted through a single column of the sample. The transmitted beam of electrons forms a high-resolution image on the fluorescent screen or through an optical image sensor like charge couple device (CCD) cameras. Image can be magnified and focused to a nano scale range. The image appears in black and white, the dense areas of the sample through which electrons cannot pass appears dark (black). The areas through which large number of electrons were transmitted...
represents less dense region of the specimen appearing bright (white). Here two types of images can be possible with beam of electrons: a bright field image obtained by transmitting electrons and the dark field image due to the diffracted electron beam. The TEM investigation provides the surface morphology and Selected Area Diffraction Pattern (SAED). The Miller indices and the crystallinity information of the samples can be evaluated using SAED pattern.

![Fig.3.6 Photograph of Transmission Electron Microscope](image)

**3.3.4 UV-Visible Spectrophotometer**

Optical absorption studies are necessary for the determination of the optical band energies of solids. The instrument contains distinct sources, monochromator, sample holders and detectors [101]. Optical absorption spectrum of the specimens has been noted using double beam UV-Visible (model V-670) spectrophotometer. The photograph and the optical alignment of UV-Visible spectrometer are displayed in Fig. 3.7 and Fig. 3.8. The spectrophotometer is capable of recording the absorption spectra in the wavelength region of 200 to 2500 nm. A deuterium discharge tube was employed as light source for use in UV region 190-350 nm. A tungsten iodine lamp is employed for use in VIS/NIR region 330-2500 nm. The light from the source lamp is reflected by a mirror into a slit to fall onto the monochromator then it is dispersed by
the grating in the monochromator and light transmitting through the exit slit is collimated. The sector mirror converts the signal into two signals.

Fig. 3.7 UV-Vis Spectrophotometer (JASCO V670)

Among these, one fall on the specimen to be evaluated and the second signal is fed to reference compound. The signal that propagated through sample or reference sample is incident on a photomultiplier tube and transformed into an electrical signal. After being synchronously refracted, the signal gets converted into a digital form and enters a personal computer which displays in the form of a spectrum. Light source change over, wavelength drive, shift drive, filter drive etc are controlled by the personal computer. The diffuse reflectance spectra have been noted in the wavelength (λ) range of 40-400 nm to find out the optical band gaps (E_{op}) for the prepared samples. With the help of the following expression: Kubelka-Munk function of reflectance F(R) can be estimated (Naidu et al., 2016 c).

\[ F(R) = \frac{1-R^2}{2R} \]  

(3.8)

The ‘α’ (absorption coefficient) is directly proportional to Kubelka-Munk function of reflectance F(R). Therefore, the expression to estimate the E_{op} can be written as

\[ (αhν)^n = A (hν - E_{op}) \]  

(3.9)

where A is energy-independent constant which depends on transition probability, E_{op} is optical band gap, n represents the type of transition i.e. n = 2 for direct transition, 2/3 for direct forbidden transition, ½ for indirect allowed transition, 1/3 for indirect
forbidden transition and $h\nu$, the photon energy. In this study $n = 2$ was taken for direct transition. $E_{op}$ values were attained by extrapolating the linear part of $(\alpha h\nu)^2$ vs. $h\nu$ curve to zero absorption coefficient ($\alpha$).

**Fig. 3.8 Optical Alignment of UV-VIS Spectrophotometer**

### 3.3.5 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy has been broadly used to identify the functional groups in organic compounds, since the fact that their spectra are usually complex and gives plenty minima and maxima which are useful for comparison. This technique is established on the fact that atoms in a molecule vibrate with respect to each other with much distinct frequencies for a given set of functional groups of atoms; the molecule is irradiated with IR radiation of various photon energies. If the energy of the photon coincides with the energy quantum required to rise a molecular vibration to next level, it will be absorbed by the molecule, where as photons of other wavelengths will
propagate through molecule. These is a possibility to get an absorption spectrum by scaling the intensity of transmitted radiation for a wide range of photon energies.

![Schematic Diagram of Fourier Transform Infrared Spectrophotometer](image1)

**Fig. 3.9 Schematic Diagram of Fourier Transform Infrared Spectrophotometer**

![Photograph of FTIR Spectrophotometer](image2)

**Fig. 3.10 Photograph of FTIR Spectrophotometer**
The Fourier transform infrared spectra (IR affinity-1, Shimadzu) of titanate powders are noted in the range 400-4000 cm\(^{-1}\) using FTIR spectrophotometer. This tool contains a mercury vapor lamp as the source, an interferometer chamber comprising KBr and a beam splitter continued by a sample chamber and a detector. The schematic diagram and photograph of FTIR spectrometer are shown in Figs. 3.9 & 3.10.

The vibrational motions of the chemically bound constituents of matter have frequencies in the IR range [103, 104]. The force constants of ‘\(v_a\)’ (A-sites) and ‘\(v_b\)’ (B-site) of the samples have been obtained by employing Waldron method. Mathematical formula is mentioned as follows

\[
v_a = 7.62 \times M_t x 2^{4} x 10^{-7} \text{ (N/m)} \tag{3.10}
\]

\[
v_b = 5.31 \times M_o x 2^{4} x 10^{-7} \text{ (N/m)} \tag{3.11}
\]

where ‘\(M_t\)’ and ‘\(M_o\)’ are the molecular weights of cations at A and B- sites.

### 3.3.6 Dielectric Measurement

The LCR bridge is mainly used for the purpose of studying the electric, dielectric and magnetic permeability properties. The photograph of HIOKI 3532 – 50 LCR meter interfaced to a PC is shown in Fig.3.11. For dielectric properties the samples are to be prepared in disc shape. The dielectric bridge contains four major parts such as LCR Bridge, PC, programmable furnace and sample holder, which was kept in a furnace. In this investigation ‘\(\varepsilon_r\)’ (dielectric constant), ‘\(\sigma_{ac}\)’ (ac-conductivity) and ‘\(\tan \delta\)’ (dielectric loss tangent) of the specimen has been reported from 1 kHz to 5 MHz range at room temperature.

Two terminal capacitance method was used to estimate the variations of dielectric loss and dielectric constant with respect to temperature and frequency. The dielectric cell employed in the current work is schematically shown in Fig. 3.12. The test sample was taken in the form of approximately 10 mm diameter and 3-4 mm thickness and was fixed between the two-nickel plated brass circular discs which act as electrodes and the two sides of the specimen disc are coated with a thin layer of conducting silver paint for providing good electrical contacts. One of the metal discs
which act as the electrodes was spring loaded to take care of the effect of thermal expansion of the specimen.

Fig. 3.11 HIOKI 3532-50 LCR Hi-TESTER for Dielectric Measurement

Fig. 3.12. Sample Holder
1. Screw arrangement for the adjustment of the upper electrode.

2. Connecting leads to HIOKI LCR Hi TESTER Model 3532-50.

3. Supporting frame

4. Ceramic studs

5. Nickel plated brass electrodes

6. Test sample

The important property of dielectric material is dissipation factor which is a measure of loss of a dielectric. When ac-signal is applied across a capacitor or a capacitive load, the voltage and current are ideally out of phase by 90°, and no power is dissipated in the capacitor. In all real capacitors the phase difference is somewhat less than 90° and power is dissipated. The loss tangent is generally considered as the tangent of the loss angle between the current and voltage vectors [105]. The change of the dielectric constant ($\varepsilon_r$) depends on the grain size effecting stress distribution in the grain as reported by [106].

The ac-electrical parameters like ‘$\varepsilon''$, ‘$\varepsilon''''$ and ‘$\sigma_{ac}$’ are evaluated using the following relations: These properties are useful for discussing the polarization phenomenon in the specimen. The ‘$\varepsilon'$’ of the sample can be measured with the help of the following relation:

$$\varepsilon' = \frac{C_p A}{\varepsilon_0 d}$$  \hspace{1cm} (3.12)

where ‘$C_p$’ = parallel capacitance, ‘$d$’ = thickness, ‘$A$’ = area of cross section of the specimen and $\varepsilon_0$=permittivity of free space ($8.854 \times 10^{-12}$ F/m). The $\varepsilon'$ of a specimen has its influences due to electronic, ionic, interfacial and dipolar polarizations in the sample, dielectric loss can be calculated using an equation:

$$\varepsilon'' = \varepsilon' \tan \delta$$  \hspace{1cm} (3.13)

The ‘$\sigma_{ac}$’ of all the samples was computed from the following relation [107]:

$$\sigma_{ac} = \omega \varepsilon' \varepsilon_0 \tan \delta$$  \hspace{1cm} (3.14)
where $\varepsilon_0 = \text{dielectric permittivity of free space}$ and $\omega = \text{angular frequency}$. The activation energy is estimated from the slope of Arrhenius plot of $\ln(\sigma_{ac})$ versus $10^3/T$ with the help of following relation:

$$\sigma_{ac} = \sigma_0 \exp \left( -\frac{E_a}{k_B T} \right)$$

(3.15)

Where ‘$E_a$’ corresponds to activation energy, ‘$k_B$’ is the Boltzmann constant and ‘$T$’ is absolute temperature.

### 3.3.7 Ferroelectric Properties & P-E Loop

Ferroelectric materials were insulators which exhibit a spontaneous polarization ($P_s$) and a domain structure. For every domain of such a ferroelectric specimen, the molecular dipoles have the similar alignment, but this alignment is varying for distinct domains and can be affected by an external electrical field (E). For ferroelectric materials, ‘$P_s$’ arises only for a particular temperature range. In many cases, ferroelectric crystals may undergo changes of their structure, therefore losing their spontaneous polarization. This structural change of those crystals and the appearance/disappearance of spontaneous polarization ($P_s$), is called a phase transition, and the corresponding temperature is called transition temperature or Curie point ($T_c$). The crystals $\text{KH}_2\text{PO}_4$, $\text{PbTiO}_3$, $\text{BaTiO}_3$, $\text{LiTaO}_3$ etc. are ferroelectric, if $T < T_c$ and para-electric, if $T > T_c$. At $T_c$ all the characteristics of the crystals like electrical, mechanical, optical, thermal etc. experience an abrupt change and many anomalies exists. The domain structure impacts numerous non-linear properties of ferroelectric specimens, with in those there is a non-linear dependence of the electrical polarization on the external field $P = P(E)$. Fig. 3.13 exhibits the hysteresis loop of a ferroelectric material, which evidences that the impact of an external electrical field lead to the rearrangement of domains (pieces). The change in electrical field causes a phase difference between the electric field intensity and the polarization, thus the non-linear variations.

When an external field affects the crystal, the domains having a polarization parallel to the increase in external field, on the account of those domains having a distinct polarization; hence, the curve a-b-c in Figure 1 illustrates the polarization rises and the dependence on $P = P(E)$. While all the domains have aligned parallel to the electric field, the polarization achieves a saturation level $P_s$; then we can ‘say that’
the crystal has become a single domain. The spontaneous polarization value was acquired by the extrapolation of the linear part in the point c. The $P_s$ value which was attained is evidently same as the polarization that occurred in every domain in the early state with respect to the point ‘a’.

![Image of P-E Loop Tracer]

**Fig. 3.13 P-E Loop Tracer**

While the intensity of the external field reduces, so does the polarization. When the external field is removed, there will remain a small amount of polarization in the crystal which is called “remnant polarization ($P_r$)”, which is denoted by the curve c-d. To abolish the remnant polarization ($P_r$), suitable part of the crystal must be polarized in the opposite direction by applying an electric field in opposite direction. The minimum field which is required to encounters the polarization, is known as “coercive field ($E_c$)”; which is shown in Figure 1 by the curve d-e. Furthermore, the polarization of the ferroelectric material varies its sense with respect to the alignment of the domains according to the new direction that is applied; this will ultimately attain its maximum value -$P_s$, shown as the point ‘f’ in Fig.1. The consequent alteration of the field in the direction of positive values will produce a dependence $P = P (E)$, this dependence is displayed by the curve f-g-h-c.