CHAPTER-3
EXPERIMENTAL TECHNIQUES AND
SAMPLE
PREPARATION
CHAPTER-3
EXPERIMENTAL TECHNIQUES AND SAMPLE PREPARATION

3.1 EXPERIMENTAL TECHNIQUES

3.1.1 INTRODUCTION

Different aspects of the materials studies in this work like structure, surface morphology, thermal, electrical, mechanical, optical etc. are studied in order to understand the physics of the materials. In order to get a better understanding of the structure property relationship of solids, various experimental techniques are used. The basic principles, preliminary descriptions and uses of important experimental methods along with the scope of the present investigation are furnished in the following sections.

The properties of materials are highly structure dependent. Structure is in turn determined by composition, heat treatment, and processing. Thus it is necessary to characterize both composition and microstructure at the highest possible resolution in order to understand material behavior and to facilitate the design of new or improved materials. Such characterization requires advanced and sophisticated methods of analysis using diffraction, microscopic, and spectrographic techniques.

3.1.2 X-RAY DIFFRACTION STUDY

a) INTRODUCTION

The X-Ray Diffraction (XRD) technique is the most important tool for studying structural properties (i.e., cell parameters, space group, atomic and thermal parameters, particle size etc.) of single crystal polycrystalline samples and thin thick films. (i.e., this technique is usually applied for identifications of
materials). Through, it is difficult to get complete and precise crystal structure with limited powder diffraction data; it is a useful and the easiest tool to obtain preliminary structural information (i.e., crystal structure, lattice parameters, particle size etc.). This technique is useful in identifying the presence of various crystalline phases in the polycrystalline materials. The interplanner distance d-value obtained from XRD pattern provides some information of the crystal structure. The X-ray diffraction profile is used to establish the atomic arrangements in the structure of the order of X-ray wavelength. For a crystal of given displacing and wavelength, the various order of reflection occur only at the precise value of angle $\theta$ which satisfies the Bragg’s condition.

$$2d \sin \theta = n \lambda$$  \hspace{1cm} (3.1)

Where $d$ = spacing between two lattice plane,

$\theta$ = angle.

$n$ = order of diffraction.

$\lambda$ = x-ray wavelength.

The powder diffraction method has the following advantages:

1) X-ray powder diffraction profile is the characteristics of a substance.

2) Each substance in a mixture produces, independently of its on pattern. It is capable of proving quantitative and qualitative analysis of the substance.

The crystalline structure of the sample is determined by x-ray diffraction using CuK$\alpha$ radiation. X-rays are a form of electromagnetic radiation that have high energies and short wavelength in order of the atomic spacing of a solid. When a beam of x-rays falls
on a solid material, a portion of this beam will be scattered in all directions. For different planes in a crystal, the differential rays follow.

\[ n\lambda = 2d_{hkl} \sin \theta \]

This equation known as Bragg’s law. The magnitude of distance equal to \( d_{hkl} \)

\[ d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \] \hspace{1cm} (3.2)

\( d_{hkl} \), interplaner spacing \( h \), \( k \), \( l \) are miller indices, \( a \) is the lattice parameter.

Some of the applications of X-ray diffraction

- The powder diffraction pattern is the characteristics of a substance.
- Each substances in a mixture product s its own diffraction pattern independent of the other.
- It describes the states of chemical combination of elements in the materials.
- The method is capable for quantitative and qualitative analysis of a substance.

b) EXPERIMENTAL

In the present study, X-diffractometer was used in which the specimen was in a sample holder on a (RIGAKU MINIFLEX) goniometer that is mounted at the center of the diffractometer and rotated by angle \( \theta \) around an axis in the specimen plane. The x-ray source was CuK\( _\alpha \) radiation. The counter is attached to an arm rotating around the same axis by angle 2\( \theta \). The diameter of the focusing circle continuously shrinks with increasing diffraction angle. Only plane, which are parallel to the specimen plane, contributes to the diffraction patterns the corresponding d-values are noted and compared.
(c) CALCULATION

The powder profile of the substance, even without further interpretation, can be used for identification of materials. For better understanding of the various characteristic features, an accurate determination of interplanar spacing (d), lattice parameters etc. is very essential. Amongst the many x-ray experimental techniques available at present, X-ray powder diffraction techniques is considered to be most simple method to provide structural information. The advantage of powder X-ray diffraction technique is as follows:

The lattice constants from the linear position or d-spacing calculated using a general formula in terms of the unit cell parameters a, b, c, α, β and γ: The accurate determination of interplanar spacing (d) of a plane (hkl) and lattice parameters (a, b, c, α, β, and γ) provides an important basis in understanding various properties of materials. The calculation of lattice constants from the line or peak positions are d spacing can be done using a general formula [1-2].

\[
\frac{1}{d^2_{hkl}} = \frac{1}{V^2} \left[ h^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta + l^2a^2b^2\sin2\gamma + 2abc \right.

\left. + kla(\cos\beta \cos\gamma - \cos\alpha) + hlb (\cos\alpha \cos\gamma - \cos\beta) \right]
\]

Where V = volume of the unit cell given as

\[
V = abc (1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2 \cos\alpha \cos\beta \cos\gamma)^{1/2}
\]

Where a, b, c. are cell dimensions, α, β, γ, are interfacial angles and h, k, l, are the Miller indices.

The above equation for d spacing reduce3s to for orthorhombic system

\[
\frac{1}{d^2_{hkl}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]
And for tetragonal systems it becomes

\[ \frac{1}{d_{hkl}^2} = \frac{(h^2 + k^2)}{a^2} + \frac{l^2}{c^2} \] .................................(3.5)

The most common and widely used powder diffraction techniques are the photographic and counter techniques [3]. The consideration of sensitivities, accuracy and simplicity, a direct measurement of intensity with the help of radiation counter is used. The powder profile is the characteristic of a material; it can be used for identification of materials even without any further interpretation. From the mastered position of a given powder diffraction line, Bragg angle \( \theta \) can be determined. By knowing the wavelength of x-ray beam used and the Bragg angle, the interplanar d-spacing of the corresponding reflecting lattice planes can be calculated.

The interpretation of powder diffraction pattern/profile can be a simple or difficult task depending upon the number of atoms present in the unit cell and the complexity of the phase composing the specimen. The simplest way to interpret the experimental data is by comparing it with the standard pattern of reference materials. For a polycrystalline material consisting of sufficiently large and strain free crystallites, the lines of powder pattern should be extremely sharp. But actually it is difficult to expect such sharp diffraction profile due to the combined effects of instrumental errors and other physical factors, which broadens the diffraction line profile [1, 3]. There are many theoretical and experimental studies on powders to obtain crystalline size and lattice strain. Scherrer’s [4], Warren- Averbach’s [5] and Wilson [6] theories are considered to be most important. When broadening of the line profile of the diffraction pattern, if it is solely due to small crystallite size, the Scherrer equation is used to calculate the mean effective or apparent crystallite dimensions \( P \) for a particular reflection \((h k l)\).
\[ P_{hkl} = k \lambda / (\beta_{12} \cos \theta) \] ...............................(3.6)

Where \( \beta_{12} \) full width at half maximum (FWHM) in radians on the 20 scale and \( k \) is a constant approximately equal to unity and related to the crystalline shape. The best possible value of \( k \) has been obtained as 0.89. Using Scherrer formula the particle size of the entire sample under investigation has been calculated. In order to eliminate the instrumental error, the value of FWHM (\( \beta_{12} \)) of the standard sample is subtracted from the \( \beta_{12} \) value of the sample:

\[ [\beta_{12}^{2 \text{ effective}} = \beta_{12}^{2 \text{ sample}} - \beta_{12}^{2 \text{ silicon}}] \]

Where \( k = 0.89, \lambda = \text{Cu-}1.5418 \text{ A}, \beta_{12} = \text{half width of peak} \).

From the powder profile \( \theta \) is calculated for each peak and the corresponding \( d \) values are calculated from the formula

\[ d_{hkl} = \lambda / 2 \sin \theta \] .................................(3.7)

The \( d \) values are used in a computer program ‘POWDMULT’ with different options of crystal systems. Calculated \( d \) values, \( hkl \) and cell parameters of the samples are obtained. A suitable crystal system was selected on the basis of best agreement between \( d_{\text{obs}} \) and \( d_{\text{cal}} \). Least square refinement method was used to obtain unit cell parameters for this matching.

Certain factors such as temperature, polarization of x-rays, scanning rate, structure factor, sensitiveness and limitations of the instrument, etc. influence the intensities of x-ray diffraction lines. The intensity of the beam diffracted from an actual crystal depends on the number, type and distribution of atoms in the unit cell. The different factors affecting the diffraction intensities can be grouped in to single expression for use in calculating the relative intensity of reflections.
The intensity of the beam diffracted from an actual crystal depends on the number, type and distribution of atoms in the unit cell. In order to calculate the intensity of a particular reflection and the relative intensities of various reflections one has to take into account the contribution of all the atoms in the unit cell to the scattered amplitude of x-ray in a given direction. For powder method, the relative x-ray intensity is given by [7].

\[ I = |F|^2 J \left[ \frac{1 + \cos^2 \theta}{\sin^2 \theta \cos \phi} \right] e^{-2M} \] ...........................(38)

In which \( \frac{1 + \cos^2 \theta}{\sin^2 \theta \cos \phi} \) = Lorentz polarization factor, \( e^{-2M} \) = temperature factor, \( F \) = structure factor and \( J \) = multiplicity factor. The factors upon which the intensity depends are described below in brief.

(1) Structure factor –

The modulus of structure factor \(|F|\) and the intensity are related by \(|F| = I^{1/2}\). \(|F|\) can be calculated theoretically if the positions of the atoms (i.e., \( x, y \) and \( z \)) in the unit cell are known using the following equation.

\[ F(hkl) = \sum f_j \exp(2\pi i (hx_i + ky_j + lz_j)) \]

Where \( x_j, y_j \) and \( z_j \) are the fractional co-ordinates and \( f_j \) is the atomic scattering factor for the \( j^{th} \) atom in the unit cell, \( N \) being the total number of atoms in the cell is in general, a complex number and its absolute value is defined as the ratio of the amplitudes.

Amplitude of the wave scattered by all atoms of a unit cell

\[ |F| = \text{Amplitude of the wave scattered by a electron at origin} \]

Structure factor thus is the manifestation of the nature of the constituent atoms and their arrangements in the unit cell.
(2) Polarization factor:-

When unpolarized rays emanate from the X-ray tube due to Rayleigh scattering of x-rays from electrons the unpolarized beam get polarized. The extent of the polarization is a function of the angle through which the beams gets scattered. The intensity of the scattered beam depends on the angle and scattered is given by

\[ I = I_0 \frac{k}{r^2} \left(1 + \cos^2 \theta \right)/2 \]

Where \( I_0 = \) intensity of the incident beam and \( k \) is a constant. The term \( (1 + \cos^2 \theta)/2 \) is known as polarization factor (P).

(3) Lorentz factor:–

If a single crystal rotates about in a plane perpendicular to the path of an x-ray beam, various planes are successively presented to the beam at their respective Bragg angles \( \theta \), so that they reflect. The rate at which a plane passes through Bragg condition depends on \( \theta \). This fact leads to the inclusion of a function called Lorentz factor \( L \), in the expression for intensity of each individual reflection. For powder specimens \( L \) can be expressed as

\[ L = \frac{(1 + \cos^2 \theta)}{\sin^2 \theta \cos \theta} \]

When \( \theta \) approaches 0° and 90°, the Lorentz factor gets its maximum value and minimum value. Therefore, this factor becomes prominent at very low and very high angle.

(4) Scale factor:–

The superposition of reflected beams, in some cases from several planes. In order to account for this increased intensity, a factor called scale factor \( J \) is introduced for determining the relative intensity. In powder diffraction techniques, the value of \( J \) depends on the symmetry of the crystalline material.
(5) Temperature factor:–

A crystal is a collection of atoms, located at fixed points in the lattice. Actually the atoms have thermal vibration about their mean position even at absolute zero temperature and the amplitude of this vibration increases as the temperature increases. The increased thermal vibration of the atoms with temperature has three major effects:

- The unit cell expands, causing a change in the interplaner spacing $d$ and hence the $2\theta$ positions of the diffraction lines,
- The intensity of the diffraction lines decreases and,
- The intensity of the background scattering between lines increases. This thermal effect is incorporated as a negative exponential of temperature.

(6) Instrumental factor:–

The instrumental factor which influences the broadening of the profile are: a x-ray source profile, (b) divergence of the beam, (c) absorption of the beam by sample, (d) width of the receiving slits and, (e) misalignment of the apparatus.

In the present structural investigation of the proposed samples, following structural parameters are obtained from XRD techniques. (i) Quality and confirmation of the prepared samples. (ii) The inter-planner $d$-spacing (iii) the intensities of the reflections (iv) the unit cell dimensions and crystal system and (v) The determination of crystallite size.

Along with the structural information, XRD analysis also provides information regarding necessary condition of ferroelectricity i.e. the absence of center of symmetry [7, 8].
3.1.3 DIELECTRIC STUDY

Ferroelectrics possess mechanical and optical effects, which are interactive with their electrical behavior in producing useful electro-chemical and electro-optic devices. Therefore, electrical properties are very much important in understanding and characterizing ferroelectrics materials. Among the electrical properties, dielectric study is most important, which provides important information regarding the ferroelectrics [9].

When a dielectric is placed in alternating electric field, a temporary phase shift is found to occur between the driving fields and resulting polarization, as a result a loss current component appears giving rise to the dielectric loss of the sample. The polarization \( P \) varies periodically with time as well as electric displacement \( D \). In general, \( P \) and \( D \) may lag behind in phase relative to the applied voltage \( E \) (a function of time).

\[
D = D_0 \cos(\omega t - \delta) = D_1 \cos(\omega t) + D_2 \sin(\omega t)
\]

Where \( \delta \) is the phase angle and slightly less than 90°.

\[
D_1 = D_0 \cos(\delta) \quad \text{and} \quad D_2 = D_0 \sin(\delta)
\]

The ratio of displacement vector to electric field \( (D_0/E_0) \) is in general frequency dependent for most of the dielectrics. Hence we can introduce to frequency dependent dielectric constants:

\[
\varepsilon' (\omega) = \frac{D_0}{E_0} \cos(\delta)
\]

\[
\varepsilon'' (\omega) = \frac{D_0}{E_0} \sin(\delta)
\]

These two constants can be expressed in terms of a single complex dielectric constant \( \varepsilon^* = \varepsilon' - j \varepsilon'' \).

Let the electric field at any instance be \( E = E_0 e^{j\omega t} \). The total current is given by

\[
I = \frac{dQ}{dt} = jC_0 E = j\omega \varepsilon^* C_0 E
\]
Where $C$ and $C_0$ are the capacitance in dielectric medium and vacuum respectively. In terms of a complex dielectric constant $\varepsilon^* = \varepsilon' - j\varepsilon''$.

$$I = j\omega C_0 E (\varepsilon' - j\varepsilon'') = \omega C_0 E \varepsilon'' + \omega C_0 E \varepsilon' = I_1 + I_2$$

The loss tangent is given by $\tan \delta = I_1 / I_2 = \varepsilon''/\varepsilon'$. The total current $I$ through the capacitor can be resolved into two components (i) a charging current $I_1$ leading the voltage by $\pi/2$ radians and (ii) a conduction current $I_2$ in phase with the voltage.

The dielectric properties of ferroelectric materials depend on the field strength at which they are measured: this is of nonlinear relation between polarization and electric field. The dielectric constant obeys the Curie-Weiss law above the transition temperature. Studies of the electrical properties of all the materials in the present work, as
functions of frequency or temperature may provide useful information regarding the existence of ferroelectricity and nature of phase transition in them. Further, based on the thermo dynamical model for ferroelectric ceramics, the following are some special features of these types of dielectrics [10].

- Under the influence of microstructure and impurities, phase transition in ceramics may be different in composition with that of single crystals.
- Dielectric constant does not change sharply in the transition region, but shows a broad peak over a wide temperature range.
- The ferroelectric Curie temperature $T_c$ or the temperature of maximum dielectric constant of a ceramic material is strongly dependent on the grain size of a material, the porosity, inhomogeneity and impurities present in ceramic.

The Curie - Weiss constant of a ceramic is higher than that of the corresponding single crystal and it depends on the dimension of the pores in the ceramic. The characterization of dielectric ceramics has received considerable scientific interest because of their enormous applications in electronics devices such as resonators, actuators, multilayer capacitors, etc [11]. The principal applications of dielectric materials are as capacitive elements in electronic circuits and electrical insulations. The relative dielectric constant ($\varepsilon_r$), loss tangent ($\tan \delta$) and dielectric strength (breakdown) are the three important characteristics of the dielectric ceramics relevant to their suitability for device application [12]. The relative dielectric constant of the material determines the ability to store electrostatic energy. The loss tangent indicates the ability of dielectrics to support the electrostatic field, while dissipating minimal energy in the form of heat. The
lower the dielectric loss (the proportion of energy loss as heat) the more effective is the
dielectric material [13]. Dielectric strength indicates the maximum voltage that the
dielectric can safely withstand. Dielectric properties depends upon the chemical
composition, structure and particle size of the material and various external factors such
as temperature, humidity, mechanical stress, intensity and frequency of the electric field
Ferroelectrics are non-linear dielectrics whose dielectric behavior charges appreciably
with change of the electric field strength and temperature. Ferroelectric ceramics play a
significant role in modern technology owing to their excellent dielectric, electro-optic,
pyroelectric, piezoelectric, elasto -- optic and electro-mechanical properties [14].
These materials are used to design high permittivity capacitors, ferroelectric memory
deVICES, pyroelectric sensors, piezoelectric transducers, PTC thermostats, actuators.
Resonators, printer logic circuit, light modulator and deflector, frequency changer, etc.
[15]. Ferroelectrics materials are considered important and useful for the following
reasons
1. High relative dielectric constant as compared to the ordinary dielectrics
2. Relatively low dielectric loss
3. High dielectric breakdown strengths
4. High specific electrical resistivity
5. Non-linear electrical behavior (hysterersis)

The measurement of dielectric parameters of the ferroelectrics over a wide range
of frequency and temperature provides some useful information regarding the existence
of ferroelectricity, the nature of phase transition and suitability of materials for device
impurities, microstructure, grain size, porosity, etc [16, 17].
Since the charge in a dielectric has both real and imaginary components (caused by their resistive leakage or dielectric absorption) the dielectric loss (loss tangent) is expressed by the ratio of the out of phase components which is called dissipation factor $D$ (frequently expressed as the $\tan \delta$ or loss tangent).

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$

Where $\varepsilon''$, $\varepsilon'$ are imaginary and real parts of the complex dielectric constant $\varepsilon^* = \varepsilon' - i\varepsilon''$

Based on the thermodynamical model of Yurkevich and Rolov [18] for ferroelectric ceramics. To obtain relative dielectric constant and loss tangent the following methods are generally used.

- **RF method (lump circuits method)** - Radio frequency range
- **Microwave method (distributed circuit method)** - at microwave frequencies
- **Impedance method** - Audio frequency range

In the present study, the impedance method has been used to investigate the dielectric properties of the compounds. In this method, capacitance of a sample is measured using impedance bridge, depending on frequency range, such as Schering Bridge, transformer ratio bridge etc. Then the relative dielectric constant ($\varepsilon_r$) of the sample is calculated from its capacitance and geometry.

The dielectric loss experiments ($\varepsilon_r$ and $\tan \delta$) of all the samples were measured at different temperatures and frequencies using a HP - LCR a laboratory made sample holder and a furnace connected to a variac. The temperature was recorded by a thermocouple (chromel-alumel) connected with a dc microvolt meter (M/S. Systronics Ltd., India) with accuracy of 0.1mV (equivalent to 2.5°C). The data were recorded in a
temperature interval of about 5°C after the sample attains steady state. Silica gel was put inside the sample holder to make the sample moisture free. The Hioki 3532 LCR HiTESTER is used to measure continuous mode impedance data. The Hioki 35322 LCR HiTESTER measures a maximum of routine test parameters such as L,C,R,Z,θ,D,etc.out of which any four can be displayed on the screen simultaneously. The frequency was adjusted freely with four digit precision in the range of 421 Hz to 5 MHz. Moreover, this impedance meter was set, not only to a floating voltage setting, but also to a constant voltage setting or a constant current setting [19].

The characterization of dielectric behavior is very important not only to the theory of the polarization mechanism but also from application point of view: where knowledge of the temperature and the frequency dependence of dielectric constant along with the frequency dependence of dielectric anomaly (if any) are very important. The measurement of permittivity and conductivity shows dielectric dispersion behavior; this offers an opportunity to gain vital insight into the details of ionic conduction processes. Particularly in solids that show dielectric polarization along with high electrical conductivity (conducting dielectrics) as it reveals the interaction of migrating ions with other defects. For all ferroelectrics, in general, the study of electrical conductivity is otherwise important as associated properties such as piezoelectricity, pyroelectricity are dependent on the order and nature of conductivity in the materials. Similarly, the electrical impedance formalism helps to understand the relaxation of defect species and dielectric behavior.

Transport and relaxation properties can be described at higher temperatures with reference to inter-particle interaction [20]. The electrical conductivity studies
indicate the nature of dominant constituent or charge species involved in the conduction on application of external electric field. Impedance spectroscopy has been applied successfully in the investigation of conducting dielectrics / ferroelectric [21]. The dielectric constant obtained from a.c. data would be unambiguous and would have a better physical significance than those obtained from capacitance measurement at chosen fixed frequencies.

3.1.4 COMPLEX IMPEDANCE SPECTROSCOPY

Complex impedance spectroscopy (CIS) is an experimental tool for the characterization of electrical properties of materials [22]. The technique is based on analyzing the a.c. response of a system to a sinusoidal perturbation and subsequent calculation of the impedance as a function of the frequency of the perturbation. The technique enables us to evaluate and separate the contribution to the overall electrical properties in frequency domain due to electrode reactions at the electrode / material interface and the migration of charge carriers (ions) through the grains and across the grain boundaries within the specimen sample.

![Figure 3.4 Representation of cell impedance (Z) on a vector diagram/complex plane.](image)
In impedance spectroscopy technique, a sinusoidal signal of low amplitude is applied across a sample and the impedance (Z) and phase shift (0) are measured directly at the output. The impedance, being a complex quantity, can be represented in vector diagram in the form of real (Z') and imaginary (Z'') components as shown in the Fig.3.4. The results of the complex impedance measurement of a sample can be displayed conventionally in a complex plane in terms of any of the following equivalent representation:

Complex impedance (∊) = Z' - jZ'' = Rs - 1/jωCs

Complex admittance, Y (∊) = Y' + jY'' = 1/Rp + jωCp - G(∊)+jB(∊)

Complex electric modulus M (∊) = 1/∊(∊²) = M' + jM'' = jωC₀Z

Complex permittivity (Dielectric constant), ε(∊) = ε' - jε''

Where, j = √-1, C₀ = vacuum capacitance of the sample, G = conductance. B = susceptance, subscripts: s for series and p for parallel combinations of the circuit elements.

Impedance analysis basically involves the display of the impedance data in different formalism and provides the maximum possible information about the materials. The display of impedance data in the complex plane appears in the form of a succession of semicircles attributed to relaxation phenomena with different time constants due to the contribution of grain (bulk), grain boundary and interface/polarization in a polycrystalline material (Fig.3.5). Hence, the contribution to the overall electrical property by various components in the material is separated out easily. In case of a solid crystalline material, the physico-chemico process and polarization events leading to the formation of double layer capacitors at the electrode-material interface take place in such a way that these
phenomena can be represented in terms of equivalent circuit representation by a series combination of parallel RC units in Fig.3.6.

Figure 3.5 Relationship between microstructure electrical properties in Complex impedance plane

Figure 3.6 An electrical equivalent circuit in complex impedance plane

Cole-Cole [23] utilized both complex plane plots and frequency explicit plots to explain the dielectric behavior and electrical conductivity of a wide range of solid-state materials. One of the main advantages of frequency dependent measurements is that the contributions of the bulk material, the grain boundaries and electrode effects can easily be separated if the time constants are different enough to allow separation [24]. The complex plane plots result in different semicircles, intercepting along x-axis (Z'-axis) at different region as shown in Fig.3.6. The intercept of the first semicircle in the high frequency region is due to grains; the second one at intermediate frequency due to grain-boundaries
and the third one in the low frequency due to electrode material. Grain resistance is evaluated in term of bulk resistance ($R_b$) as the intercept of high frequency semicircle on $Z'$ - axis.

The peak of the semicircle in the complex plane plot enables us to evaluate the relaxation frequency ($f_{\text{max}}$) of the (bulk) material in accordance with the relation,

$$\omega_{\text{max}} \tau = \omega_{\text{max}} R_b C_b = 2\pi f_{\text{max}} R_b C_b = 1$$

$$f_{\text{max}} = 1/2\pi R_b C_b \text{ and } \tau = 1/2 \pi \ldots f_{\text{max}}$$

Where $R_b$ = bulk resistance, $C_b$ = bulk capacitance and $\tau$ = relaxation time.

The impedance data also enable us to investigate the information on relaxing dipoles in the material (dielectric relaxation spectroscopy) in terms of the real and imaginary parts of the complex dielectric constant $\varepsilon = \varepsilon' - j\varepsilon''$ through the relations:

$$\varepsilon' = -\frac{Z'}{\omega C_0 (Z'^2 + Z''^2)}$$
$$\varepsilon'' = -\frac{Z''}{\omega C_0 (Z'^2 + Z''^2)}$$

The real and imaginary arts of complex electric modulus represented as:

$$M' = \omega C_0 Z'' \text{ and } M'' = \omega C_0 Z'$$
$$\tan = \varepsilon''/\varepsilon'$$

Where $Z'$, $\varepsilon'$, $M'$, and $Z''$, $\varepsilon''$, $M''$ are real and imaginary parts of impedance, dielectric constant and electric modulus, respectively. $\omega = 2\pi f$, is the angular frequency and $C_0 = \varepsilon_0 A / l$ = geometrical capacitance of the sample.

The impedance measurements in the present studies were carried out using a computer controlled Hioki LCR HiTESTER (Model: 3532, Japan) as a function of frequency (100Hz to 1MHz) and temperature (about 250 to 500°C). The main purpose to study electrical properties of the proposed materials using variable frequency measurements is
to assign the different electrical impedance to appropriate regions of the samples (i.e., for bulk, grain boundaries, electrode-material interface etc.) and extract maximum amount of useful information from the acquired data namely relaxation frequency, activation energy, ac and dc conductivity values etc.

3.1.5 A.C. ELECTRICAL CONDUCTIVITY STUDY

Electrical conduction in dielectrics is caused due to ordered motion of weakly bound charged particle under the influence of electric field. When an alternating emf, V is applied across a capacitor an alternating current I will flow through it provided that the dielectric is perfect one [25]. In general, however, an in phase component of current will appear corresponding to a resistive current between the condenser plates. Such current is entirely due to dielectric medium and is a property of it. The ac conductivity of the dielectric can be deduced from the real part of current density passing through it. The ac conductivity (\(\sigma_{ac}\)) and activation energy (\(E_a\)) of the compounds in the high temperature (i.e., in paraelectric phase) were calculated from dielectric data using Arrhenius equation:

\[
\sigma = \sigma_0 \varepsilon_0 \tan\delta = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad \text{(where } \varepsilon_0 \text{ is the vacuum dielectric constant, } \varepsilon \text{ the angular frequency and } k \text{ the Boltzmann constant.)}
\]

The dc (bulk) electrical conductivity, evaluated from the impedance spectrum using the relation,

\[
\Sigma_{dc} = \frac{1}{R_b A}
\]

Where \(R_b\) = the bulk resistance obtained from the low frequency intercept of the real \(Z'\) axis in the complex impedance plot, \(l\) = the sample thickness and \(A\) =area of the sample surface.
3.1.6 BASIC THEORY OF FT-IR AND RAMAN SPECTRA

Systematic studies of Vibrational spectra (FT-IR and Raman) in the systems containing molybdenum and tungsten have been carried out in this work. Raman spectroscopy is regularly used to study the effects of incorporating a large diversity of materials, for example of interest for catalysis and alkaline and rare earth elements. Fourier Transform IR spectra in combination with Raman spectra using group theoretical techniques allow the assignment of vibrational modes in different crystalline environment. Thus the effect of alkali cation substitution and site potential can be deduced by analyzing and comparing the modes in various materials of double alkali molybdates/ tungstates family [26-30].

Factor group analysis is used to understand the number and symmetry of internal and external vibrational modes in each material and detailed assignments of observed Vibrational modes is made.

1. Effect of cation size effect on the vibrational modes and use them as an aid to assign the external lattice modes.

2. Investigate the observed vibrational modes in room temperature vibrational spectra and the effect of crystalline structure on the observed mode.

3. Effect of site symmetry on the internal modes and its coupling with other modes for analyzing the nature of distortion in tetrahedral/ octahedral molecular species in these materials.

4. To corroborate the reported crystal structural results as their are discrepancies in reported results and in some cases crystalline structure is not reported.
3.2 SAMPLE PREPARATION

One chief concern in the application of ceramic materials is the method of synthesis as many of the operation of ceramics rely on fabrication techniques employed [31-32]. Ceramics is composed of an aggregate of randomly oriented crystallites intimately bonded to form solid. In fact, ceramics can be considered as a substitute for single crystals due to following reasons –

1. Ceramics are easier to fabricate into different shapes and sizes that the single crystal counterparts.

2. Ceramics have an additional structural feature -the microstructure. The microstructural feature can be exploited in the design of electro- ceramic materials for particular device requirements. The presence of grain boundaries gives rise to additional effect which is not present in single crystal. Some of the mechanical properties of ceramics like hardness high temperature strength and creep resistance are microstructure dependent.

3. Ceramics have the advantage of thermal chemical and mechanical stability. Hence it becomes important to tailor the microstructure of the components as required for the application of ceramics. Under several operating conditions these feature may justify the use of ceramics in spite of their brittle non-ductile characteristics [33-37].

3.3 GENERAL METHOD FOR PREPARING CERAMIC SAMPLES

A number of preparation methods both physical and chemical have been developed to prepare ceramics materials.
(A). **physical method**: - many physical methods may be used for sample preparation. Some of the important ones are

**Melt spinning technique**: This technique is very useful for the preparation of two phase ceramic material in which one phase is coupled to other. Starting materials consists of three to five elements which on heating in some inert atmosphere give an alloy ingot. These ingots are then gushed into small pieces for melt spinning. Quartz crucibles are used for this purpose. Spinning equipment with copper roll in an inert atmosphere. The amorphous ceramic samples have to be sealed in an evacuated quartz tube annealed for various periods. This technique has minimum interface contamination and can produced almost porosity free samples. annealing conditions alloys, control over grain size and the technique can produce large quantities of the desired ceramics materials.

**High energy ball mill method**: - This method is used for the preparation of nanocrystalline materials. Nanostructure is obtained by repeated mechanical deformation and alloying as a powder is vigorously shaken in a vial containing a number of milling ball. The energy transfer take place by a shearing action or impact of the high velocity ball with the powder.

The size of the nanoparticles depends on several factors namely milling speed, size distributions of balls to powder weight ratio, milling atmosphere. This process has a advantage to produce large quantities of material and is already a commercial technology contamination of ball that should be taken care of.

1. **Sputtering technique**: - This process involves acceleration of ions of element like argon or crypton to high energies and their bombardment into target materials atoms and cluster; both neutral and ionic particles are ejected from the target. For materials with low
mutual solubility, co-sputtering is more effective, contamination problem is less as sputtering is performed under high vacuum small cluster formation is a drawback for sputtering. Various sputtering parameter like environment and also annealing of the sputtered film can be used to tune the grain size.

1. **Glass Ceramic Method:** - Glass ceramics are produced by controlled crystallization of appropriate glass. Two stage heat treatment programs are performed to precipitate various non- crystalline phases in the parent glass system. The glass specimens are subjected to heat treatment at nucleation and crystallization temperature respectively. Crystallization temperature is obtained from differential thermal analysis curve. Nucleation temperature is calculated after knowing the glass transition temperature from DTA curve. Nanoparticles remain well protected within the glass matrix.

2. **Molecular Beam Epitaxy Technique:** - This is a technique in which epitaxial layers are grown over a heated substrate by impinging molecular or atomic beams evaporated from effusion sources under ultrahigh vacuum conditions. It differs from conventional vapor deposition technique in that the beam intensities of each source and the substrate temperature separately controlled to achieve epitaxial growth. MBE has become a very important growth technology not only for semiconductors but also for other material systems like metals, insulators and superconductors. The greatest advantage of these techniques is a highly precise control of larger thickness.

(B). **Chemical Method:** - Some chemical methods are also used for sample preparation. These methods are:

1. **Sol–gel method:**

   The sol-gel process is a wet-chemical technique for the fabrication of materials (typically
a metal oxide) starting either from a chemical solution or colloidal particles to produce an integrated network. Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form a colloid, a system composed of solid particles (size ranging from 1 nm to 1 μm) dispersed in a solvent. The sol evolves then towards the formation of an inorganic continuous network containing a liquid phase. Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution. The drying process serves to remove the liquid phase from the gel thus forming a porous material, and then a thermal treatment may be performed in order to favor further polycondensation and enhance mechanical properties.

The precursor sol can be either deposited on a substrate to form a film (e.g. by dip-coating or spin-coating), cast into a suitable container with the desired shape (e.g. to obtain a monolithic ceramics, glasses, fibers, membranes, aero gels), or used to synthesize powders. The sol-gel approach is interesting in that it is a cheap and low-temperature technique that allows the fine control on the product’s chemical composition, as even small quantities of dopants, such as organic dyes and rare earth metals, can be introduced in the sol and end up in the final product finely dispersed. It can be used in ceramics manufacturing processes, as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes. Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio) sensors, medicine and separation technology.
2. Co-precipitation method: -

Precipitation of multi-component system is known as co-precipitation. This process involves formation of a solid precipitation followed by the separation of a solid with a filtration step. This process needs a co-precipitation agent which can be a solution of inorganic or organic salt. The main condition is that the compound should be insoluble in the mother liquid. Parameters like mixing rate, pH, temperature concentration etc. have to be properly adjusted. Drying and subsequent annealing require to prepared nano-structured materials by this method.

3.4 SOLID STATE METHOD

This method is very useful for homogeneous powder processing. We formed the ceramic by the method of mixed oxide process of high temperature solid-state reaction. This method is used for the sample preparation and has following steps-

1. Weighting and Wet mixing: - Taking proper stoichiometric amounts of raw materials of samples is an important aspect of ceramic preparation. If ‘$m$’ be the molecular weight of desired material and ‘$m_a$’ be the molecular weight of the $a^{th}$ metallic oxide used in synthesis in which ‘$z$’ fraction of metallic ion present then the weight required for $m^{th}$ metallic oxide is given by

$$M_a = m m_a z / M$$

Mixture is called solid solution. Homogeneity should be there in solid solution otherwise the properties of the ceramic specially the dielectric properties are degrade. For better homogeneity wet mixing is preferred.
2. **Grinding**: - It can be accomplished by any suitable process either by an agate mortar and paste or ball milling. Grinding brings homogeneity and helps to adjust compositional variations, which may arise during calcinations.

   Generally ceramic have large intergranular voids of low density. It the precursors are intimately mixed the colloidal properties may interface with forming steps.

3. **Calcinations**: - After thorough mixing the materials are calcined that is heated to form the required single-phase material. Calcinations is high temperature solid state reaction carried out at temperature usually less then that of fixed firing temperature. Calcination or presintering can also be described a process in which the power in heated to about \((2/3)^{th}\) of its melting point for several hours.

4. **Grinding (After Calcination)**: - After calcined sample grinding can be accomplished by any suitable process either by an agate mortar pastel or ball milling. Grinding brings homogeneity and helps to adjust compositional variations, which may arise during calcination.

5. **Role of Binder**: - The raw materials are mixed with a binder 2\% (PVA) solution and then pressed to desired shape Binder brings better compactness among granules of the materials and get volatile during sintering.

6. **Pelletization**: - The calcined powder was again ground to very fine powder. This powder was used to make cylindrical pellets by applying high pressure \(3.10^9\) N m\(^{-2}\) using a hydraulic pressure Polyvinyl Alcohol (PVA) was added to the powder which acts as a binder. The pressure was maintained constant.

7. **Sintering**: - during firing the formed piece shrinks, this is due to sintering. During the initial sintering stage such forms along the contact regions between adjacent particles and
also a grain boundary is formed. As sintering progress the pores becomes smaller. Sintering is carried out below the melting temperature so that a liquid phase is not present.

8. **Powder Pressing**: - There are three basic powder-pressing techniques:

   a) Uni-axial.

   b) Isotactic.

   c) Hot pressing.

In our experiments we are using uni-axial method. In this method the powder is compacted in a metal die by pressure that is applied in single direction. This formed piece takes the configuration of die and plates through which the pressure is applied. Advantages of this method are high production rate and inexpensiveness.

9. **Electroding**: - To carry the studies on electrical properties of sintered samples one need to electrode the sample by some suitable conducting materials as silver, gold graphite etc. While electroding the following points should be taken care of:

   a) The material should add with the sample.

   b) The material should have almost zero contact resistance.

   c) It can be pasted in the form of thin layer.

   Gap between the electrode and the face of the pellet should be avoided because it will affect the properties of sample.

   Electrode adherence is critical on the smooth ceramic pellet. The sintered pellets are polished with fine emery paper to make both the faces flat and parallel. These pellets were coated with high purity conducting silver paste for all electrical measurements.
3.5 PREPARATION OF THE MATERIALS

Ceramic samples of NLM (NaLiMoO₄), KLM (KLiMoO₄), RLM (RbLiMoO₄) and CLM (CsLiMoO₄) and their tungsten analogs were prepared by high temperature solid state reaction route. Starting Materials were high purity Na₂CO₃, Rb₂CO₃ and Cs₂CO₃ (AR grade, Loba Chem. 99.9%), M/s. S.D. Fine Chem. India), Li₂CO₃ (AR Grade Loba Chem. 99.9%), and WO₃/ MoO₃ (AR Grade Sigma 99.9%), M/s. BDH Chemical UK) using high temperature solid state reaction route as per the reaction. 0.5 M A₂CO₃ + 0.5 M B₂CO₃ + 1 M WO₃/MoO₃ = ABWO₄ / ABMoO₄ + CO₂ , Where A = Na, K, Rb, Cs....., B = Li, K....were prepared from pure oxides/carbonates. Similarly, rare earth substituted alkali molybdates and tungstates also prepared RE³⁺ (MoO₄/WO₄)₂ ceramics are (RE³⁺ = Sm³⁺, Eu³⁺). Thallium substituted materials were obtained commercially.

The stoichiometric amount of carbonates and oxides were thoroughly mixed in agate mortar for 2 hours. The respective mixtures were calcined in alumina crucible at 500°C for 16 hours. The calcined powder was grinded for one hour to make fine powders. The process of grinding and calcination was repeated to ensure the formation of the material phase. The quality and the formation of single phase material were checked by XRD technique. The fine and homogeneous powder of the prepared materials were pressed into cylindrical pellets of 10 mm diameter and 1-2 mm thickness under a uni-axial pressure of 5×10⁶ N/m² using a hydraulic press. Polyvinyl alcohol (PVA) was used as a binder to reduce the brittleness of the pellets. The pellets were then sintered for 12 hours at 550°C in air Atmosphere. The binder was burnt out during the sintering. Crystal structure of the sintered powder was studied by an X-ray diffraction technique (XRD). The sintered pellets were polished with fine emery paper and then coated with high purity air
dried conducting silver paste. The pellets were dried at 150°C for about 4 h. The synthesis process flow chart is shown in figure 3.7

Flowchart

Start

Starting Materials or Precursors

Mixing and grinding /drying

Calcination (500°C) (In covered alumina crucibles)

Cooling at room temperature

Drying

Add binder Polyvinyl alcohol (PVA)

Pelletization

Sintering (550-600°C)

X-ray Diffraction

End

Figure 3.7 Flow chart for sample preparation and XRD.
REFERENCES


