

## *Chapter 2 Experimental Procedure*



Chapter 2 gives a detailed description of the techniques used for synthesizing the materials and various experiments employed for its characterization.

This part begins with the procedural description and steps required in the synthesis of various materials such as, Ti, Al and Co substituted BFO solid solution and their composite with terbium magnetites ( $\text{TbMnO}_3$ ), which is followed by different experimental technique utilized for the estimation of various properties of the desired materials.

### **2.1 Experimental Techniques**

In the present work, the standard solid state reaction method has been used for the synthesis of polycrystalline BFO solid solution and its composite. Generally, for the preparation of BFO and its composites this method is most commonly used. This method is commenced by mixing the suitable highly pure (99.9%) oxides in respective stoichiometric ratios. It is generally observed that oxides show very low reactivity at room temperature and so the reaction do not take place at this temperature; external heat is needed to initiate the reaction among them. The thermodynamic free energy change is needed to determine the reaction mechanism. The reaction between the solids depends on the concentration of the reactants, activation energy, reaction condition, structural and surface area of the solids. The schematic flow chart showing the reaction kinetics of various steps in the synthesis of the samples by solid state route is shown in the Figure 2.1.

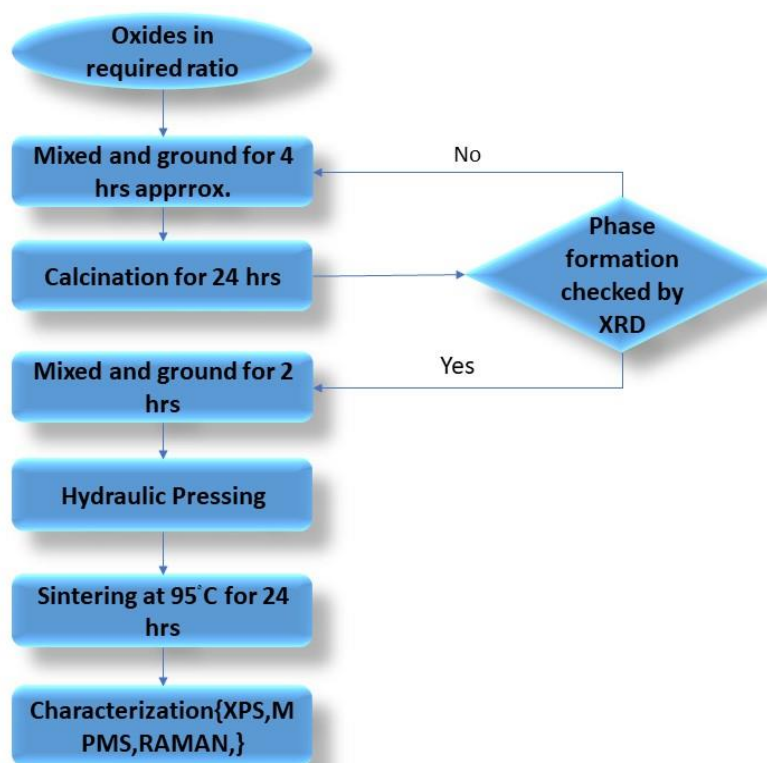


Figure 2.1 Flow chart of solid state method.

In our research work, we have used highly pure oxides are used as source materials for chemical synthesis. The proper stoichiometric ratio of oxides is weighed and mixed in dry, followed by wet mixing with acetone as a medium in an agate mortar. The mixed powder was then calcined at different temperatures in a programmable air furnace to vanish agglomeration of particles. After cooling to room temperature, calcined powder was grounded into the fine powder to detect phase formation at room temperature by using powder X-ray diffraction (PXRD) technique. The obtained calcined powder was again grounded and pressed by compacting it into a pellet shape using the hydraulic press under suitable pressure, for sintering. The sintered samples were carried out through different aspects of material characterization techniques, for example, structural, optical, magnetic, electrical etc. which is discussed in detail below.

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## 2.2 Characterizations Techniques and Their Working Principles

This study investigated the working principle and importance of different experimental and characterization of samples like structural, magnetic and electrical properties.

### 2.2.1 X-ray Diffraction Technique

X-ray diffraction (XRD) is most fundamental, non-destructive techniques for studying the structure of the crystalline materials. Since the various properties of materials (optical, magnetic, electrical, etc.) are related to the atomic arrangement of the chemical species. Therefore, crystal structure information is successfully used for the characterization of solids for device application. In the XRD technique, monochromatic X-ray radiation typically copper source ( $\text{Cu-K}\alpha = 1.5418\text{\AA}$ ) are used for the identification of unknown crystal structure. When a collimated beam of X-ray strikes the sample in powdered form maintained on a glass slab, diffraction occurs for all the desired value of  $2\theta$ . The beam diffracted from the sample is collected by employing a moveable detector such as a Geiger counter, a scintillation counter or image plate which is linked to the chart recorder. X-ray diffraction set-up is illustrated in Figure 2.2. In regular use, the counter is driven to scan at a constant angular velocity over a range of  $2\theta$  values. In general, powder XRD data is collected in a range of  $10$  to  $90^\circ$  which is enough to get the required information of our powdered sample. The identification of single or multiple phases allows us an understanding of the mechanism behind the formation of the sample. The electromagnetic radiation interacts with the periodic structure to form a characteristics diffraction pattern. The distance of the periodic structure should be the same as the wavelength of the radiation. It happens because X-ray wavelength is of the order  $1$  angstrom ( $10^{-8}$  cm) which is the same as the

order of the inter-atomic distance of the crystalline solids. The X-ray beams incident on a crystalline solid will be scattered from it, producing diffraction pattern by constructive interference.

### 2.2.1.1 Bragg's Law

The angle at which a beam of X-ray of a particular wavelength will be reflected from a crystalline surface is given by a relation derived by the English physicists Sir W.H. Bragg and his son Sir M. Lawrence Bragg and is known as Bragg's law

$$2d \sin \theta = n \lambda$$

$n$  = Integer representing the order of diffraction

$\lambda$  = wavelength of the incident X-rays

$d$  = Interplanar spacing

$\theta$  = Angle of incidence

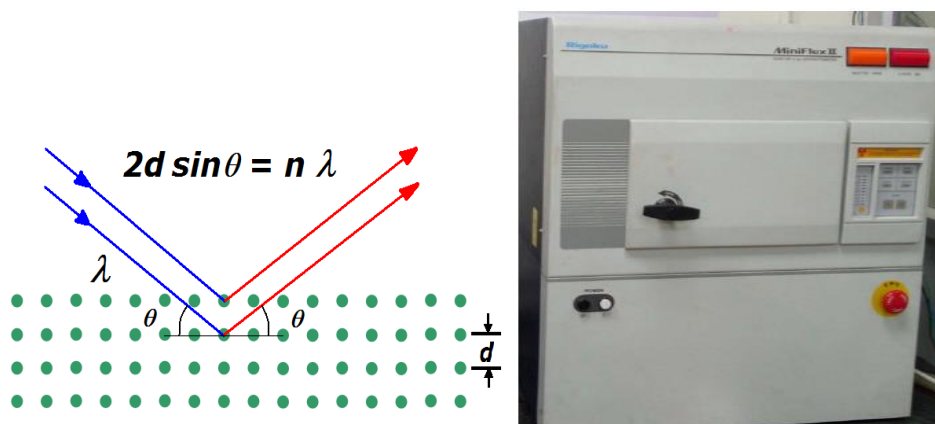


Figure 2.2 The phase formation of prepared samples has been studied by using Rigaku-MiniFlex-II DESKTOP powder X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) at 30 kV and 15 mA. Crystal structures of each composition were recorded at  $2\theta$  angle between  $20$  and  $80^\circ$  with a step size of  $0.02$ . X-ray diffraction analysis revealed all the important parameters such as crystalline structure, lattice parameters, unit cell volume, atomic packing fraction etc.

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### 2.2.2 Raman Spectroscopy

Raman spectroscopy is a process employed to know about the vibrational, rotational, and low-frequency modes of the sample. The data/spectrum obtained in this technique is the result of inelastic scattering of monochromatic radiation. The lasers used as a monochromatic light source is usually in the visible, near infrared, or near ultraviolet range.

In Ramanspectroscopy, laser light of particular wavelength is focused on the specimen which interacts with molecular vibrations or other excitations of the system. Due to this interaction, there is a change in energy of the laser photons either by increasing it (shifted up) or decreasing it (shifted down). The shift in energy (Raman shift) gives an information about the vibrational and /or rotational modes in the system. Reinshaw Raman spectrometer equipped with a 532nm laser can be used to collect the Raman spectra of samples at room temperature as shown in the Figure 2.3. The pump source i.e. diode-pumped solid-state laser (DPSSLs) of wavelength 532nm having a maximum power of 100 mW, 5% of which have been used to avoid laser-induced heating in the materials. The incident laser beam comes to a focus at a very short working distance over a 50× long-distance objective linked to the Leica DM 2500M microscope. As a dispersion element 2400 grooves/mm grating is installed and to maintain the constant phase the slit width of 50 micron is kept fixed all through the measurements. The radiation after scattering is collected at back scattered position which is passed through the filter to eliminate the un-useful part of radiation. After which the radiation is fed to the detector. The resolution of the spectrometer is more than  $1 \text{ cm}^{-1}$  with deviation from the ideal spectrum less than  $\pm 0.2 \text{ cm}^{-1}$ . Using the supplied 4.0 software Spectrometer scanning, data collection, and processing were done.

### 2.2.2.1 Selection rule

The polarizability ( $\alpha$ ) can often be used to determine the charge distortion of the electron cloud of an atom or molecule, placed in the electric field. The Raman shift can be activated optically if the first derivative of the polarizability ( $\alpha$ ) with respect to the normal co-ordinate (Q) has a non-zero value

$$\frac{\partial \alpha}{\partial Q} \neq 0$$

Generally, a laser beam (monochromatic source) is used to illuminate the sample which is in the ultraviolet(UV), visible(Vis) or near-infrared(NIR) range. Radiation from the illuminated spot is collected by lens and focused on a monochromator. Wavelengths corresponding to the Rayleigh scattering arising due to the elastic collision are filtered out while the rest of the collected light is dispersed onto a detector.

Raman effect takes place when electromagnetic radiation is focused on a molecule and it interacts with electron cloud and bonds of that molecule inelastically. In case of spontaneous Raman effect, atom or molecule are excited from the ground state to virtual energy state. Molecule being unstable at virtual energy state emits a photon to achieve stable state by decreasing its energy and returns to a different rotational or vibrational state. There is energy difference between the initial state of the molecule (before the interaction of radiation) and the final state which leads to a shift in the emitted photon's frequency away from the excitation wavelength. If the final vibrational state of the molecule is more energetic than the initial state, then the emitted photon will be shifted to a lower frequency so that the total energy of the system remains balanced. This shift in frequency is referred to as stoke shift name after Irish physicist



George Gabriel Stokes. When the emitted photon has less energy than the absorbed photon, then the emitted photon will be shifted to a higher frequency, and this is designated as an Anti-Stokes shift. Raman spectra are typically reported in wave numbers, which have units of inverse length ( $\text{cm}^{-1}$ ). Moreover, the spectral wavelength can be converted into wavenumber of the shift in the Raman spectrum through the following equation:

$$\Delta w = \left( \frac{1}{\lambda_0} - \frac{1}{\lambda_1} \right)$$

Here,  $\Delta w$  is the Raman shift in term of wavenumber,  $\lambda_0$  is the excitation wavelength, and  $\lambda_1$  is the Raman spectrum wavelength.

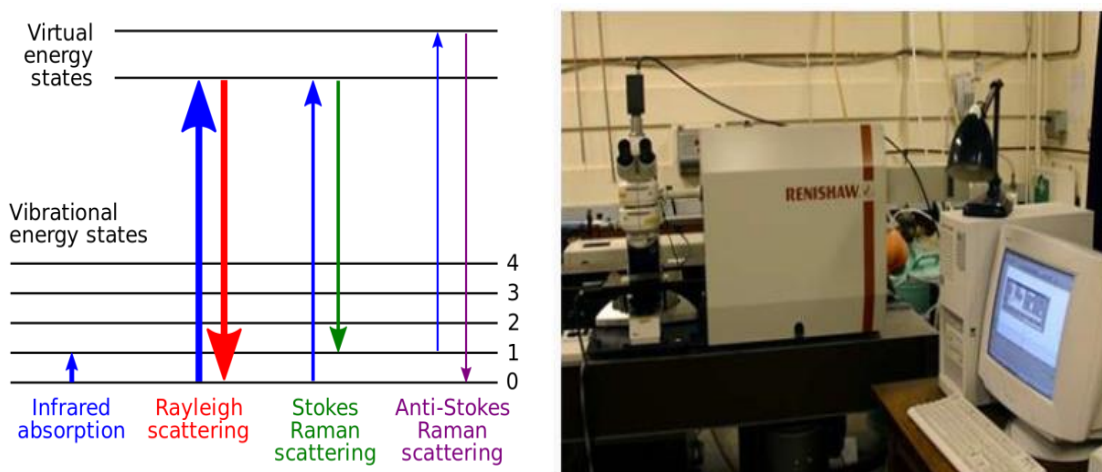


Figure 2.3 (a) Energy level diagram showing states involved in Raman signal. The line thickness is roughly proportional to the signal strength from the different transitions. (b) Renishaw micro Raman spectroscopy.

### 2.2.3 Ultraviolet-visible (UV-Vis) spectroscopy

UV-Vis spectroscopy is concerned with absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. The UV-Vis spectrum can be used to determine the absorption of the particular wavelength as well as calculate the band gap of the material. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. All molecules will undergo an electronic transition in the region of the electromagnetic

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spectrum. It determines the intensity of light passing through a sample ( $I$ ) and compares it to the intensity of light before it passes through the sample ( $I_0$ ). The ratio  $I/I_0$  is called the transmittance, which is sometimes expressed as a percentage and referred to as % transmittance (%T)

$$\% T = \frac{I}{I_0} \times 100$$

From the transmittance or % transmittance, we can describe the absorbance ( $A$ ). Absorbance is the amount of light absorbed by a sample. It is calculated from T or %T using the following equation:

$$A = -\log(T/100)$$

The UV-visible spectrophotometer can also be applied to determine the reflectance of the sample. In this case, the intensity of light reflected from a sample ( $I$ ) is measured by the spectrophotometer, and then it compares with the intensity of light reflected from a reference material ( $I_0$ ) (such as a white tile). The reflectance is described as the ratio of  $I/I_0$  and is usually expressed as a percentage (%R).

The essential parts of a spectrophotometer are a sample holder, a diffraction grating used as monochromator to separate the different wavelengths of light, a light source, and a detector.

Diffraction gratings are used with CCDs, which collect lights of different wavelengths on different pixels. The radiation source is often a Tungsten filament (300-2500 nm), a deuterium arc lamp which is continuous over the ultraviolet region (190-400 nm), and more recently light emitting diodes (LED) and Xenon Arc Lamps for the visible wavelengths. The detector is typically a photodiode or a CCD. Photodiodes are used with monochromators, which permit only light of a single wavelength to reach the detector. UV-Vis spectrophotometer has been used for nanoparticles as well as a liquid sample.



Figure 2.4 UV-Vis.set up.

#### **2.2.4 Magnetic Property Measurement System (MPMS)**

Quantum Design MPMS 3 magnetometer can be used to study the magnetic properties of the sample. MPMS provides three possible measurement modes, DC scan mode, AC susceptibility mode and vibrating sample magnetometer (VSM) mode. In the present work, we have used VSM mode to study the magnetic properties of multiferroics samples. The recorded data provides information about the magnetic order of material using magnetization and susceptibility curve. The VSM operates on Faraday's law of induction which states that an alternating magnetic field will cause an electric field and vice-versa. In VSM operation, a material is placed within a uniform magnetic field. When the magnetic material is placed in a constant magnetic field, they get magnetized by aligning the magnetic domains in the direction of the field. The magnetization increases with increasing the magnetic field. The magnetic dipole moment of the sample will induce a magnetic field near the sample, known as a stray magnetic field of the sample. When the sample is moved up and down, this stray magnetic field is changing as a function of time. This change can be sensed by a set of pick-up coils. The changing magnetic field will

induce an electric field in the pick-up coils which is proportional to the changing magnetic flux through the coils according to Faraday's Law of Induction. This induced current is directly proportional to the magnetization of the sample. The magnetization increases with increasing the induced current. The induction current is amplified using a trans-impedance amplifier and a lock-in amplifier. The various components are connected to computer resources. Controlling and monitoring software can be used to determine how much the sample is magnetized and its behavior on the strength of the constant magnetic field. A standard measurement of a sample is used in the following manner:

- The strength of the constant magnetic field is fixed.
- The sample begins to oscillate.
- the received signal from the probe is converted into a value proportional to the magnetic moment of the sample
- No data is taken during this time.
- The magnitude of the constant magnetic field gets its new value
- The signal from the probe is again converted into a new value for the magnetization of the sample
- The constant magnetic field changes over a given range and a graph of magnetization (M) vs. magnetic field strength (H) is obtained.

Quantum Design MPMS-3 magnetometer operates in the 5-300 K temperature range, shown in Figure 2.5.



Figure 2.5 MPMS3 set up.

### 2.2.5 Ferroelectric Hysteresis Measurement

The temperature dependent ferroelectric hysteresis i.e., P-E loops of the multiferroics materials in this work were carried out using a Precision workstation of Radiant Technology. One of the standard methods for measuring spontaneous polarization is the Sawyer and Tower method, as shown in Figure 2.6.

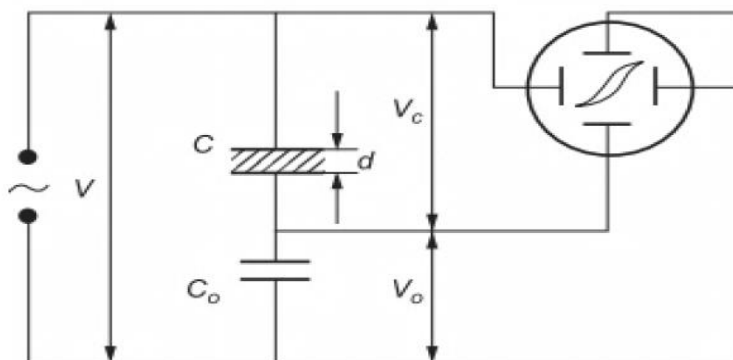


Figure 2.6 A Sawyer-Tower circuit for the measurement of ferroelectric hysteresis loop.

Where,  $C_o$  is the standard capacitor.

$C$  is the capacitance of the ferroelectric specimen.

$V_o$  is voltage across standard capacitor ( $C_o$ ).

$V_c$  is the voltage across  $C$ .

The voltage across  $C$  should be sufficiently large to render a saturation in polarization, so  $V_o$  should be proportional to the polarization charge,  $V_o = AP/C_o$ , where  $A$  is the area of the specimen and  $P$  is the polarization,  $V$  is the applied voltage which is generally an AC signal voltage of low frequency. So, the applied field across the specimen is  $F = V_c/d = (V - V_o)/d$ . Further, it is remarkable here that the P-E hysteresis loop measurement at higher frequency exhibit true polarization.

## 2.2.6 Magneto-Dielectric Measurement

In order to understand the indirect magneto-electric (ME) coupling of the multiferroic material, magnetodielectric (MD) measurement was performed on this study. The MD measurements were done by using a vibrating sample magnetometer (VSM Lakeshore model 142A) and a Keysight

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E4980A Precision LCR meter. The measurement of dielectric parameters (capacitance(C), dielectric loss ( $\tan\delta$ ), impedance (Z), phase angle ( $\phi$ )) at the different magnetic field ( $0 \leq H \leq 1.5$  Tesla) for all samples in a frequency range 100 KHz to 1MHz up to room temperature.

### 2.2.7 X-Ray Absorption Spectroscopy (XAS)

XAS (X-ray absorption spectroscopy) is a well-known and widely used analytical technique for studying the local geometry and electronic structure of matter in different scientific fields. XAS spectrum is acquired by changing the energy of the photons to a range where it can excite the core electrons. It is done by using a crystalline monochromator. The energy range lies between 0.1–100 keV or 16–16, 022 J. The edges named on the basis of which level the core electron is excited from: the principal quantum numbers  $n = 1, 2,$  and  $3,$  refers to the K-, L-, and M-edges, respectively. For example, the energy of the photon corresponds to the energy of a shell of the atom. (K, L<sub>I</sub>, L<sub>II</sub>, L<sub>III</sub>, etc. corresponding to the creation of electron holes in the 1s, 2s, 2p<sub>1/2</sub>, 2p<sub>3/2</sub> etc. atomic sub-shells) shown in Figure 2.7. The XAS follows the quantum mechanical selection rule, as it is a type of absorption spectroscopy, to select the symmetry of the final state. In XAS there are electric-dipole allowed transitions (i.e.,  $\Delta\ell = \pm 1$ ) to unoccupied final states, for instance, the most important contribution of a K-edge are due to excitation of an electron from the core transitions to vacant 1s  $\rightarrow$  p-like final states, whereas the most substantial contribution for the L<sub>3</sub>-edge are due to transition from 2p  $\rightarrow$  d-like final states.

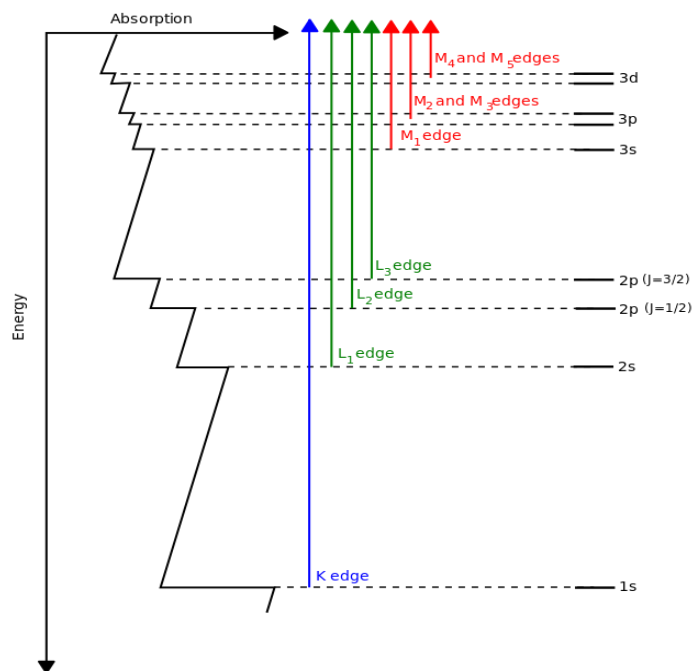


Figure 2.7 Transitions that contribute to XAS edges.

The Figure 2.8 shows the different experimental apparatus of modern XAS beam line. Mirrors are used for collimating and focusing the beam while apertures and slits define its size. A double crystal monochromator is used to choose X-ray of minimal energy, which is given by the Bragg diffraction  $n\lambda = 2d \sin \theta$ . where,  $n$  is the order of reflection (integer),  $\lambda$  represents wavelength X-rays,  $d$  stands for the distance between the atomic spacing of the diffracting crystal and  $\theta$  exhibits the angle under which the beam is incident on the crystal.

Some of the higher energy states have to be eliminated from the beam which satisfies the Bragg condition for  $n \geq 2$ . These are known as harmonics. This can be accomplished by slightly detuning of monochromator which reduces the transmission of harmonics significantly more than that of the primary energy. Moreover, the X-ray mirror system can also be used as an alternative to reflect energies below a critical value.



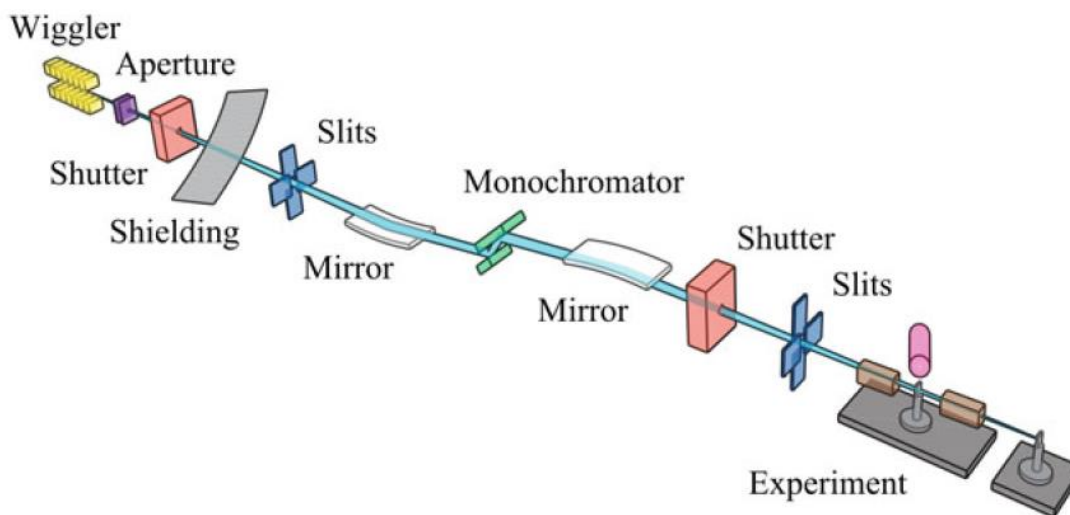
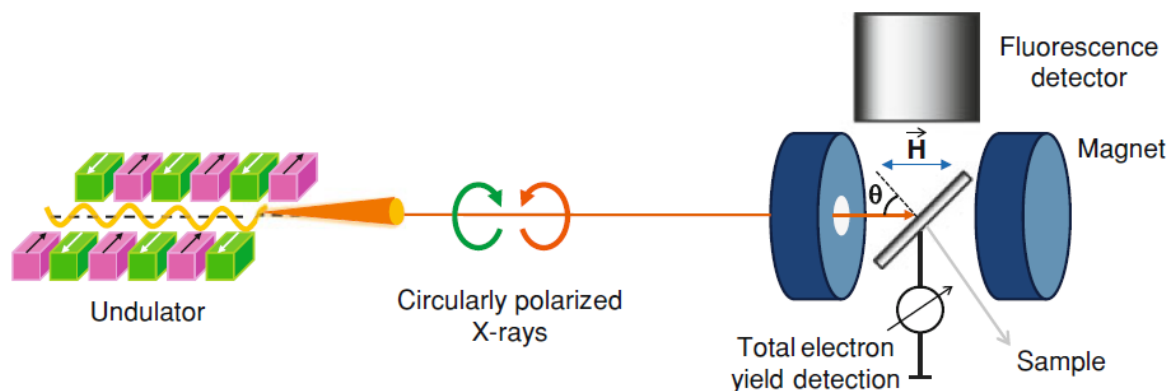


Figure 2.8 Typical components of modern XAS beamline.

### 2.2.8 X-ray magnetic circular dichroism (XMCD)

XMCD spectroscopy is defined as a difference between the two XAS spectra. These two XAS spectra are obtained from left circularly polarized light and right circularly polarized light, in the presence of magnetic field. Using this technique the information about the magnetic properties of the atom, in particular about their spin and orbital magnetic moments obtained.

A schematic view of two beamlines XMCD experimental setup is shown in Figure 2.9. The sample is positioned at the center of a superconducting magnet, which is illuminated with polarized and monochromatic X-ray. The magnetic field is applied along the direction of the incoming beam. The observation of the polarized dependent X-ray absorption spectra is achieved by fluorescence yield (FY) or total electron yield (TEY). Later is regularly used in the soft X-ray regime. The fluorescence detectors are (single - or multi-anode) ion-implanted silicon photodiodes, which are characterized by high efficiency in the X-ray range, fast time response, excellent linearity, and nearly insensitivity to magnetic fields.



**Figure 2.9:** Basic diagram of the XMCD measurement.

### 2.2.9 Dielectric analysis

The dielectric spectroscopy is the most versatile experimental technique used to characterize the insulating and semiconducting materials to prove different phenomena such as electric conduction, dipolar ordering, and dipolar relaxation. The dielectric value obtained from the measurement can be expressed in real and imaginary parts  $\epsilon^* = \epsilon' + i\epsilon''$  of the electrical permittivity. The  $\epsilon'$  ( $\epsilon''$ ) is known as real(imaginary) permittivity and both depends on various physical parameters like temperature, frequency, pressure, electric/magnetic field etc. There are several dielectric mechanisms connected to dielectric spectroscopy. Impedance spectroscopy (using  $Z^*$ ) and Electrical relaxation spectroscopy (using  $M^*$ ) are altogether co-related; experiments measure ( $Z^*=1/\sigma$ ) in all the cases.

In this research work, dielectric measurement was carried out using a Keysight E4980A Precision LCR meter. It is a standout, amongst the most impedance analyzers in the field of dielectric spectroscopy, having extraordinary precision and sensitivity of the estimated parameters.

### 2.2.9.1 Working Principle of the analyzer

The specimen is usually set in the middle of two metal electrodes, framing a parallel-plate type setup. For the measurement, the specimen is energized by an alternating signal  $V_s(f)$  with the help of a voltage generator, and the current  $I_s(f)$ . The phase shift is measured across the sample with two phase-sensitive voltmeters. The impedance  $Z^*$  is to be determined by the Ohm's law

$$Z^* = \frac{V_s(f)}{I_s(f)}$$

The observed sample impedance is linked to the sample capacitance as follows.

$$C^* = \frac{-i}{2\pi f Z^*}$$

Furthermore, from here the dielectric permittivity is resolved ( $\epsilon^* \epsilon' - \epsilon'' = \frac{C^* d}{\epsilon_0 A}$ )

### 2.2.10 Complex Impedance spectroscopy

Complex Impedance spectroscopy methods are widely used to study electrical properties of materials with their different microstructural contribution such as grain, grain boundary and corresponding interfaces over a wide range of frequency and temperature. The impedance technique measures the ac response of a system to a small sinusoidal perturbation and following that it estimates the impedance as a function of the frequency. The impedance plot in the complex plane shows up a progression of half circles, ascribing the relaxation phenomena with various time constants corresponding to the presence of grain (bulk), grain boundary and interfacial polarization in a polycrystalline. Consequently, the contributions to the overall electrical property by different electrical phenomena in the material are isolated out effectively.

AC electrical information might be connected to in any of the four fundamental formalisms which are interconnected to one another

$$\text{Complex impedance: } Z^* = Z' - iZ''$$

$$\text{Complex admittance: } Y^* = (Z^*)^{-1}$$

$$\text{Complex permittivity: } \epsilon^* = (j\omega C_0 Z^*)^{-1} = \epsilon' - j\epsilon''$$

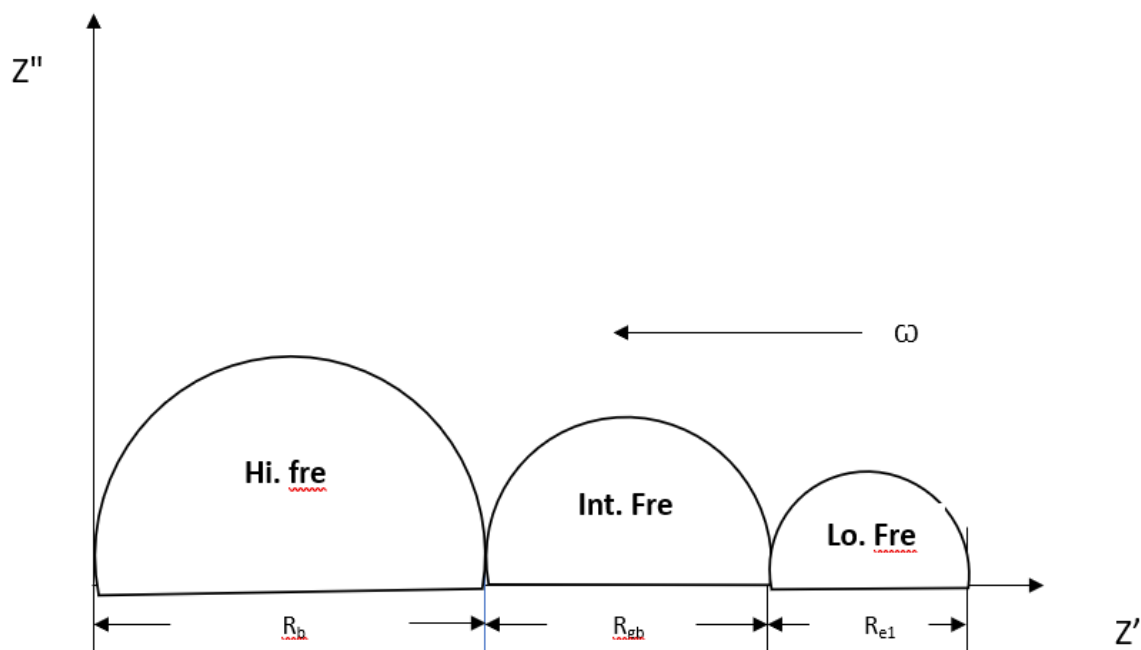
$$\text{Complex modulus: } M^* = j\omega C_0 Z^* = M' + jM''$$

Here,  $i = \sqrt{-1}$ , the imaginary factor,  $\omega_0 = 2\pi f$  is angular frequency and  $C_0 = \epsilon_0 A/d$  is the vacuum capacitance of the cell without the sample.  $A$  and  $d$  are the sample effective area and thickness respectively.

Sometimes, it is hard to interpret the data whether the response is because of long-range conductivity (delocalized) or dipole relaxation (localized) of materials. Both localized and delocalized conduction are bulk processes, and both offer the same equivalent geometrical capacitance. The imaginary part of the impedance ( $Z''$ ) and conductance ( $Y''$ ) is especially used for resistive as well as conductive investigation (when the long-range conductivity is predominant) whereas, the imaginary part of the permittivity ( $\epsilon''$ ) and electrical modulus ( $M''$ ) are reasonable when localized relaxation dominates. For multiferroic materials, a combination of all the impedance formalisms is the best way to recognize the ferroelectric and non-ferroelectric properties of the materials.

There are a few different ways of exhibiting the data, and the most widely recognized are as per the following (a) plots of the real and imaginary components is in the form of logarithmic or in linear coordinates as a function of the frequency, (b) polar plots of the imaginary component against the real component on a linear presentation.

The type of relaxation can be defined by the shape of the plot as Debye, Cole-Cole, Cole–Davidson and furthermore as a method for finding the equivalent circuit for the material. The connection between microstructure and electrical properties can be deduced from the complex impedance plot. The impedance spectrum is described by the presence of semicircular arcs because of various electrical microstructural contributions. The semicircular arc in the low frequency is usually attributed to the contribution of the electrode-material interface, intermediate frequency semicircular arc is due to the contribution grainboundary, and at high-frequency semicircular arc is because of the bulk response of the material, as appeared in Figure 2.10.



**Figure 2.10.** Relationship between microstructure-electrical properties in complex impedance plane and an electrical equivalent circuit in complex impedance plane. The intercept of the semicircular arcs on the real axis gives rise to the corresponding resistances such as Bulk, GB and interfacial.

