Chapter-II

Experimental Methods and Characterization Techniques

2.1 Introduction

In this chapter, I have discussed the synthesis process for materials and different characterization techniques used for studying the various properties of materials. Barium Strontium Titanate (BST) ceramic has been synthesized using sol gel combustion technique. BST/PVDF composite has been synthesized in compact pellet form using cold sintering process with polymer as a filler and ceramic as a matrix. Barium Zirconate and Barium Zirconate Titanate has been synthesized using high energy ball milling process and has been used as a filler in PVDF based composites. Hydroxylation of the filler has also been performed. BZ/PVDF and BZT/PVDF composite films have been synthesized using solution casting process with PVDF as a matrix. Hydroxylation of the BZ and BZT filler has also been performed and composites have been synthesized with these hydroxylated fillers to compare the properties with PVDF based composites using without hydroxylated filler. I have also synthesized pure PVDF film using same process as composites to compare the properties with pure PVDF polymer.

The properties of above synthesized materials were studied using different characterization techniques. X-Ray diffraction pattern of synthesized samples were recorded with the help of Rigaku Miniflex X-Ray diffractometer. Fourier transform infrared spectroscopy (FTIR) was performed using Alpha Bruker Eco-ATR. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed for PVDF based polymer composites to study the thermal stability of the composites using DSC-60 plus, M/s Shimadzu pvt. Limited under nitrogen atmosphere. Microstructural and elemental analysis of BST/PVDF composites were performed using high resolution scanning electron microscope (HR-SEM, FEI, NOVA NANOSEM 450). The dielectric properties were studied for BST/PVDF composites using air dried silver paste with the help of Novocontrol Alpha-A high performance frequency analyzer with varying temperature at frequency range of 1 MHz to 1kHz. The data was collected using Win-data software. The dielectric properties of composite films were studied using Keysight B2912A precision source/Measure unit (SMU). The electroded composites with the help of air dried silver paste were further characterized for Polarization vs Electric field hysteresis loop with the help of Radiant technology precision premier-II materials. The dielectric breakdown strength measurements were performed for synthesized composites using AC test setup for dielectric breakdown strength measurement and Weibull analysis were performed to obtain the average dielectric ac breakdown strength of the composites.

2.2 Materials

2.2.1 Materials used for BST/PVDF composites

Barium Nitrate (Ba $(NO_3)_2$, LOBA Chemie, 99% pure), Strontium Carbonate ($SrCO_3$, Sigma Aldrich, 98 % pure), Titanium Isopropoxide ($C_{12}H_{28}O_4Ti$, Sigma Aldrich >97% pure), Citric acid monohydrate ($C_6H_8O_7$.H2O, Qualikems > 97% pure), Ethanol (C_2H_5OH, 99.9%.), Nitric Acid, Poly(vinylidene Fluoride) (PVDF) [Alfa Aesar].

2.2.2 Materials used for BZ/PVDF composite films

$BaCO_3$ [Alfa Aesar, 99.8 %] and ZrO_2[Alfa Aesar, 99.5 %] have been used as raw material for synthesis of $BaZrO_3$ ceramic nanoparticles. Polyvinylidene fluoride (PVDF) [Alfa Aesar], N, N Dimethyl formamide (DMF) [Merck], H_2O_2 [Merck,50 %] and BaZrO3 (BZ) nanoparticles have been used as primary reagent for the synthesis of PVDF/BZ and PVDF/hy-BZ nanocomposites.

2.2.3 Materials used for BZT/PVDF composite films

Polyvinylidene difluoride (PVDF) [Alfa Aesar, density 1.78 g/cm^3], $BaCO_3$ [Alfa Aesar, 99.8%], ZrO_2 [Alfa Aesar, 99.5%], TiO2 [Thomas Baker, 99.9 %], N,N Dimethyl formamide (DMF) [Merck] and H_2O_2[Merck, 50%] were used as primary materials for the synthesis of PVDF/BZT4 and PVDF/h-BZT4 nanocomposite films.

2.3. Synthesis Methods

2.3.1 Synthesis of nanofiller

In this present research work, we have synthesized nanofiller using two following different methods.

2.3.1.1 Sol gel combustion technique

The combustion synthesis method requires using a saturated aqueous acidic precursor solution having required metal salts, along with a suitable organic fuel (such as glycine, urea, citric acid, etc.). This mixture is heated until the precursor ignites, initiating a self-sustaining and relatively rapid combustion reaction which results in typically a crystalline, dry, and fine powder. To create a complex mixed oxide, a combination of the precursor with the necessary metal ions in the form of easily soluble salts in water (e.g., nitrate salts) and a fuel like glycine, urea, or citric acid can be employed. While these redox reactions are exothermic, an uncontrolled reaction could lead to an explosion if a larger quantity of reactants is used. The combustion of mixtures of metal nitrates and organic fuel typically occurs as a self-propagating and nonexplosive exothermic reaction when dealing with smaller quantities. During the auto-ignition process, a significant amount of gases is released which results in a flame that can reach temperatures exceeding 1000°C for a brief duration. The main role of fuels used are as follows:

a) They act as sources of H and C which produce CO_2, H_2O and release heat upon combustion.

b) They form complexes with the metal ions, facilitating the uniform mixing of cations in the solution.

Metal nitrates disintegrate into metal oxides when heated to or above the phase conversion temperature through simple calcination process. In this case, a stable external heat source is crucial to maintain the system at the high temperature necessary for achieving the suitable phase transition or decomposition. In the combustion synthesis technique, the energy released from the exothermic reaction between the nitrates and the organic fuel that typically ignites, rapidly heats the system to the required temperature and sustains it long enough for the production process to occur.

The basic concept of combustion synthesis methods originates from the principles of thermochemistry commonly applied in the field of explosives and propellants. It is crucial to clearly identify the optimal composition of the fuel and oxidizer mixture to ensure a balanced calculation of oxidizing and reducing valences in the system. Jain et al. introduced a straightforward approach to estimate the nature of the mixture's reduction to oxidation [124]. This method involves a direct valency balance technique, regardless of whether the elements are present in the fuel/reducer or oxidizer components of the combination. The goal is to determine the stoichiometric composition of the redox combination that maximizes the energy released during the combustion reaction.

2.3.1.2 High Energy ball milling process

High-energy ball milling is a mechanical processing method that uses a rotating drum with balls (such as steel, ceramic, or pebbles) as grinding media to powder materials. It is a versatile and powerful technique used in materials science and nanotechnology for producing a wide range of materials with tailored properties. Researchers and engineers often optimize the process parameters to achieve the desired characteristics in the final product. High-energy ball milling is a technique used to reduce the particle size of various materials, create fine powders, and prepare nanomaterials. The process involves the use of a ball mill, a type of mechanical grinder, in which the material to be ground is placed in a container along with one or more grinding balls. The ball mill is subjected to high-energy collisions that cause the particles to break or deform.

The basic idea is to create high-energy collisions between the balls and the powder inside the milling chamber, leading to the mechanical alloying or reduction of particle size. The milling apparatus typically consists of a cylindrical container that rotates around its axis. The container is filled with the powder to be milled, the grinding balls and grinding media. As the container rotates, the balls impact and grind the material, causing it to fracture and undergo mechanical deformation. The high-energy collisions result in a combination of mechanical alloying and particle size reduction.

High-energy ball milling is often used to produce nanocrystalline or amorphous materials. The process can break down larger particles into smaller ones, leading to a reduction in grain size. This process is also used for the production of alloys by introducing different elements into the powder mixture. The repeated collisions and mechanical treatment lead to the mixing of the components at the atomic level. The process can produce powders with a high degree of uniformity in terms of particle size and composition.

The milling process can introduce impurities from the milling media or the container material. Therefore, it's crucial to carefully select materials to minimize contamination. The high-energy collisions can generate heat and if not controlled, this can affect the properties of the final product. The milling time, rotational speed, ball size, and the ratio of ball to powder are crucial parameters that can be adjusted to control the outcome of the process. Safety measures are important due to the high energy involved in the process. This may include emergency stop buttons, protective enclosures, and other safety features. Image of high energy ball milling instrument and mechanism of high energy ball mill instrument is shown in Fig. 2.1.

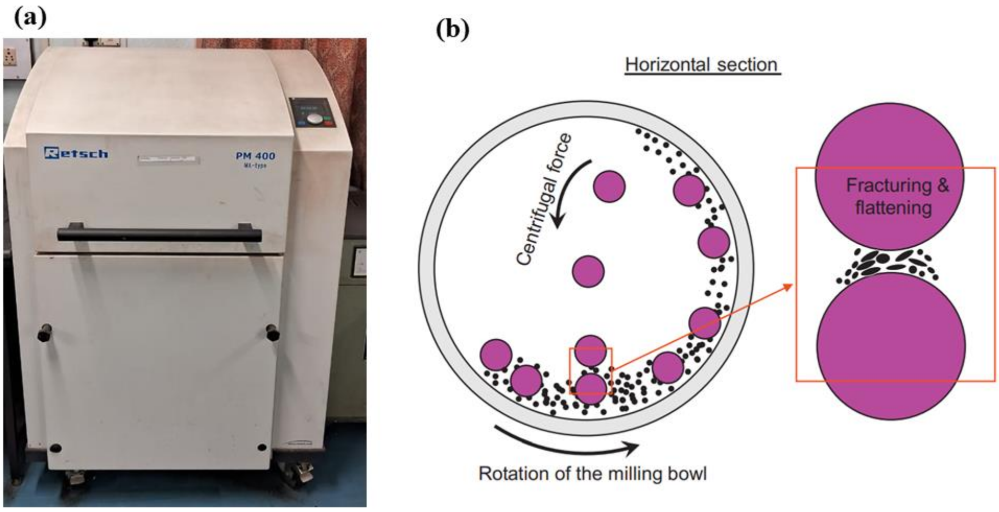

Fig. 2.1 (a) Image of High energy ball milling instrument, (b) Mechanism of high energy ball mill instrument [125].

2.3.2 Hydroxylation process of nanoparticles

The hydroxylation is the process by which -OH group can be added to the surface of nanoparticles so that nanoparticles can be dispersed uniformly in the polymer matrix to make better polymer-based nanocomposites [126]. In this process, surface of the nanoparticles became modified, thus called surface modified nanoparticles. Hydroxylation can be performed using hydrogen peroxide (H_2O_2). For hydroxylation of nanoparticles, H_2O_2 and nanoparticles were taken in a flask and heated at 106 ^{0}C for 6 hrs by closing the mouth of flask with the help of aluminum foil followed by drying it at 120 ^{0}C in an oven. Thus obtained dried nanoparticles is known as surface modified nanoparticles and can be used as nanofiller.

2.3.3 Synthesis of PVDF based polymer nanocomposites

PVDF based polymer nanocomposites have been synthesized mainly using cold sintering method in pellet form and solution casting method in thick film form.

2.3.3.1 Cold Sintering technique

Cold sintering is a relatively new and innovative technique in the field of materials science to consolidate powders at significantly lower temperatures as compared to traditional sintering methods. Traditional sintering processes typically involve high temperatures, which can be energy-intensive and may limit the materials that can be processed. Cold sintering is designed to occur at temperatures well below the melting points of the materials involved, often at or near room temperature. This process typically involves the use of a solvent or a combination of solvents that facilitate the densification of the powder compact. The solvent promotes mass transport and particle rearrangement at much lower temperatures than would be required for traditional sintering.

The process takes place at temperatures significantly below the melting points of the materials, often at or below 200 ^{0}C. The use of a solvent or a combination of solvents is a crucial aspect. The solvent helps in reducing the activation energy for diffusion and facilitates densification. The mechanism of densification can vary, but it often involves dissolution, diffusion, and precipitation processes. The solvent plays a key role in these mechanisms.

Cold sintering has been explored for a range of materials, including ceramics, polymers, composites, and more. It is particularly useful for materials that are sensitive to high temperatures or for creating composites with disparate melting points. The main advantages of cold sintering include energy savings, the ability to process a broader range of materials, and the potential for novel material combinations. This method is particularly beneficial for the sintering of ceramics that are challenging to process at high temperatures While cold sintering shows promise, challenges include finding suitable solvent systems, optimizing processing conditions, and ensuring that the resulting materials have the desired properties.

Materials synthesis procedure using cold sintering process is as follows:

Start with fine powders of the material of interest. Mix the powders with a suitable solvent or binder to create a slurry. Shape the slurry into the desired form, creating a "green body" or a compacted precursor of the final material. The green body is subjected to relatively low temperatures, typically below 300 ^{0}C. The sintering is facilitated by the application of pressure, which helps in particle rearrangement and bonding. The use of pressure reduces the need for high temperatures. As the process involves a solvent or binder, it is crucial to remove it after sintering. This is often done through drying. The material undergoes a final densification process, achieving the desired level of density and mechanical properties.

The cold sintering process (CSP) is an extra-ordinary low temperature (~ 200 ºC) liquid phase assisted sintering process that utilizes water or other volatile liquids as a transient liquid phase for mass transport for densification under a uniaxial pressure up to some Mpa range [127–129]. In a typical cold sintering process, the ceramic nano-powders are uniformly mixed with water or other suitable liquids so that the corners/sharp edges of solid surfaces of ceramics dissociates and partially get dispersed in aqueous solution forming controlled amount of liquid phase ceramic suspension at the particle-particle interfaces [130–134]. The dissociation of sharp edges of ceramics reduces the effective interfacial areas which results in minimization of the surface free energy, reduction in the porosity, and finally, better densification at lower sintering temperatures. Under simultaneous pressure and temperature, there is redistribution of the liquid phase itself filling the pores among the particles [127]. Solid particles rearrange themselves very rapidly when we apply a uniaxial pressure in the presence of liquid phase that results in the better initial densification of ceramics. With heating precipitation happens through water/ liquid phase evaporation that results in the supersaturated state of the liquid phase at a low temperature about above 100 ºC. Thus, it is the sintering condition of the Cold sintering process by which we can cosinter thermoplastic polymers and ceramics in a single-step process and get dense samples in comparison to the composite film with polymer matrix [129]. Thus pressure, evaporation temperature, and dissolution cum precipitation process play a vital role during the cold sintering process [131]. Schematic representation of cold sintering process is shown in Fig. 2.2.

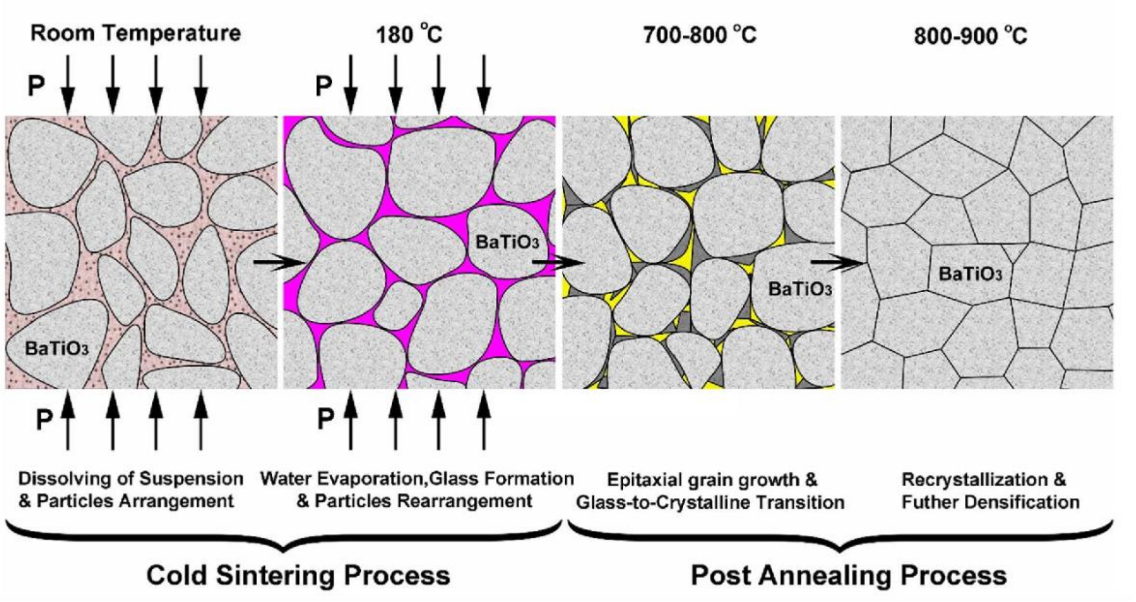

Fig. 2.2 Schematic representation of Cold sintering and Annealing process in case of $BaTiO_3$ nanocrystalline ceramic synthesis [129].

2.3.3.2 Solution Casting Method

In materials science or chemistry, solution casting is a method used to produce thin films or coatings. The basic process of solution cast method is as follows:

A solution is created by dissolving a substance (eg. polymer or a metal salt) in a solvent. The choice of solvent and concentration are critical factors in the process. The solution is then cast or spread onto a substrate or surface. This can be done using various methods, such as spin coating, dip coating, or blade coating, depending on the specific requirements of the application. The solvent is allowed to evaporate, leaving behind a thin film of the dissolved substance on the substrate. The rate of solvent evaporation can affect the final characteristics of the film. As the solvent evaporates, the dissolved substance undergoes phase separation or solidification, leading to the formation of a thin film. In some cases, additional steps like heat treatment or other post-processing may be required to enhance the properties of the film.

In this process, I have poured PVDF polymer in DMF solvent to disperse the polymer in solvent to make partially or fully soluble solution. Fillers were also dispersed in same DMF solvent to make mixture or suspension in another beaker [135]. The dispersed nanoparticles were mixed in the solution of polymer for necessary time at magnetic stirrer and then solution is casted on petri disc and dried in an oven. Nanoparticles were first probe sonicated to avoid aggregation inside the polymer solution and then used as nanofiller. This method has some advantages which involves cost effective, better uniformity of thickness, low temperature synthesis, significant diversity in film thickness and suitable for large scale production.

2.4 Characterization techniques

2.4.1 X-ray diffraction (XRD) pattern

The crystalline structure and crystallographic phase analysis of all type of crystalline materials can be performed using powder X-ray diffraction (XRD) technique. Crystallographic phases can be identified in case of unknown samples using X-ray diffraction pattern. In XRD instrument, coherent beam of incoming X-rays are incident on sample and are scattered from the parallel planes of atoms inside a crystal. The wavelength of X-rays and atomic spacing of crystals are of same order so X-rays are used to examine the structural properties of crystal. When the X-rays are incident on a material, it becomes scattered in all the directions. The x-ray diffraction pattern is observed because of interference of coherent x-rays scattered from different lattice planes of crystalline materials. When there is constructive interference between monochromatic X-rays scattered at same angles from every set of lattice planes in a crystalline material, peaks are observed in the XRD pattern of specimen. The phenomena of constructive interference are observed only when the path difference between two or more coherent X-rays scattered from different parallel planes is equal to the complete multiple of wavelength of X-rays.

The principle of powder X-ray diffraction is based on the scattering of X-rays (Electromagnetic waves) through the sample followed by diffraction. The various characteristics of the crystalline materials are examined using Bragg's law by relating the structure of crystalline materials to diffraction of X-rays. Mathematically, Bragg's law can be represented by $2d\sin\theta = n\lambda$, where d is the interplanar distance, θ is the scattering angle of X-rays, n is the order of diffraction and λ is the wavelength of X-rays used. We know that the maximum value of Sin θ is equal to 1 so the value of $\lambda \leq 2d$. Thus we can conclude that the wavelength should not exceed two times of interplanar spacings of atoms for diffraction pattern to be observed. Different peaks in the X-ray diffraction pattern are matched with the help of peak position with available standard file data (JCPDS file) to identify the crystal structure and crystallographic phase of crystalline materials. Newly prepared samples can be characterized by XRD pattern.

In general, while recording XRD pattern, the sample is kept stationary and mounted on rotation axix but detector and X-ray source rotates along its periphery simultaneously by θ angle. In some cases, sample and detector are rotated by θ and 2θ respectively while keeping X-ray source stationary. The XRD pattern between angle (2θ) range 10^0 - 80^0 is enough to determine the phase and crystalline structure of crystalline solid. The phase identification of synthesized samples has been performed by X-ray diffractometer (RIGAKU smart lab and Miniflex) using Cu-K_α radiation in angle (2θ) range of 10^0 - 80^0 at room temperature. The XRD pattern has been recorded at scanning rate of 2^0/min by applying 40kV voltage and 15 mA current. Representation of Bragg’s law for X-Ray diffraction and Image of the XRD instrument is shown in Fig. 2.3.

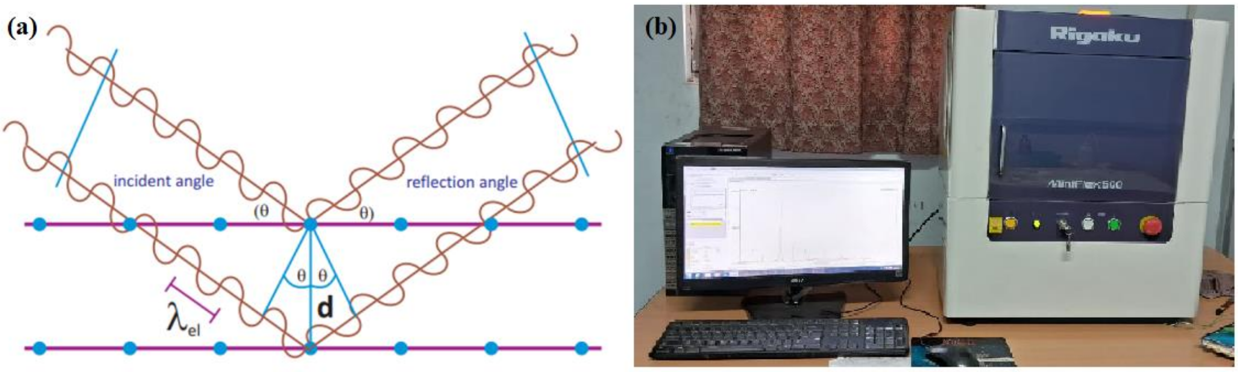

Fig. 2.3 (a) Bragg’s law for X-Ray diffraction, (b) Image of the XRD instrument

2.4.2 Fourier transform infrared spectroscopy (FTIR)

Fourier Transform Infrared (FTIR) spectroscopy is a technique which is used for the characterization and identification of chemical compounds based on their absorption of infrared radiation. It provides information about the chemical composition, molecular structure, and bonding characteristics of a sample by measuring its interaction with infrared light. FTIR is widely used in various scientific and industrial applications, including chemistry, biology, pharmaceuticals, materials science, and environmental analysis. The working principle of FTIR are as follows:

FTIR spectroscopy is based on the interaction of matter with infrared radiation. Molecules selectively absorb distinct infrared frequencies, inducing vibrational transitions. The obtained spectrum offers insight into the molecular composition and structure of the sample. In a typical FTIR spectrometer, infrared light from a broad-spectrum source is passed through an interferometer. The interferometer induces modulation in the infrared light, generating an interferogram. The interferogram is then subjected to a Fourier transform, converting it into a spectrum that represents the intensity of infrared light at different frequencies. The resulting FTIR spectrum is typically displayed as percent transmittance or absorbance plotted against the wavenumber (reciprocal of wavelength) in units of cm^{-1}. Samples for FTIR analysis are often prepared as thin films or in the form of pellets with a suitable matrix. Liquid samples can be analyzed directly, and gases can be measured in gas cells. The FTIR instrument measures the absorbance or transmittance of infrared light as a function of wavenumber (or frequency). The spectrum obtained shows distinct peaks at particular wavenumbers, corresponding to molecular vibrations present in the sample. Unique functional groups in molecules absorb infrared radiation at specific frequencies. For example, the O-H stretch in alcohols typically occurs around 3300 cm^{-1}, while the C=O stretch in carbonyl compounds is often observed around 1700 cm^{-1}. The overall pattern of peaks, sometimes referred to as the "fingerprint region" (usually 1500-500 cm^{-1}), provides a unique signature for each compound. Spectral interpretation involves identifying the peaks and comparing them to reference spectra or databases to determine the functional groups and compounds present in the sample. Software tools are often used for spectral analysis and library matching. FTIR is used to identify the functional groups and chemical composition of organic and inorganic materials. In industries such as pharmaceuticals and polymers, FTIR is employed for quality control of raw materials and finished products. FTIR can be used to analyze air pollutants, water contaminants, and soil components. In biochemistry, FTIR is used to study proteins, nucleic acids, and lipids. FTIR is applied in forensic science for the analysis of trace evidence. FTIR spectroscopy is a versatile and non-destructive analytical tool, making it valuable for a wide range of scientific and industrial applications. Mechanism and Image of FTIR instrument is shown in Fig. 2.4.

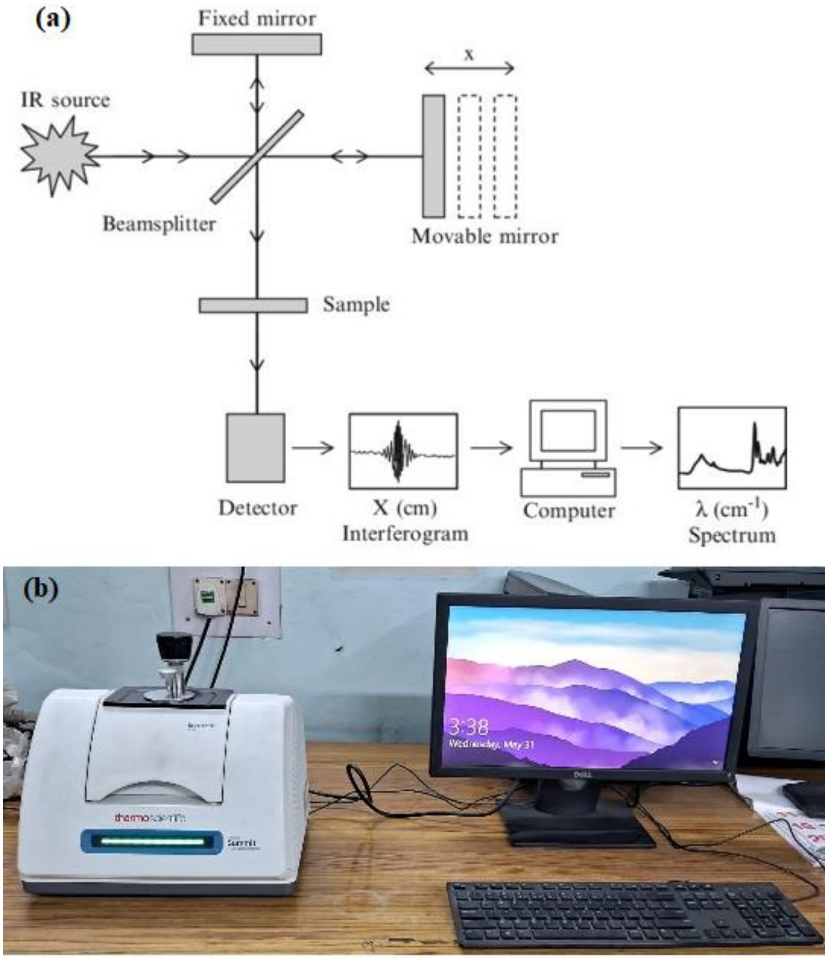

Fig. 2.4 (a) Mechanism of FTIR, (b) Image of FTIR instrument

2.4.3 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis is a technique which is used to explain the thermal decomposition of materials. It assesses alteration in the mass of a specimen over time in response to temperature variation. This occurs when the specimen undergoes a controlled temperature program in a controlled environment. TGA is widely used to investigate the thermal stability, composition, and decomposition kinetics of materials. The basic working principle of thermogravimetric analysis are as follows:

A small amount of the sample (~ a few mg.) is placed in a crucible. The sample may be in the form of pure substance, mixture or a composite material. The crucible containing the sample is placed in a specially designed furnace which is equipped with a highly sensitive balance that can measure the mass of the sample with high precision. Then, the temperature of the furnace is programmed to increase linearly with time and rate of the temperature change can be monitored. As the temperature of the sample increases, the sample undergoes various thermal events like decomposition, phase transitions or chemical reactions. The change in mass of the sample is continuously recorded using the balance. The resulting data is a thermogravimetric curve, which plots mass change (loss or gain) with temperature/time. The obtained thermogravimetric curve provides valuable information about the thermal stability of the sample and its composition. Peaks or slopes in the curve correspond to specific thermal events. By analyzing these features, we can determine the temperatures at which decomposition or other reactions take place, the amount of weight loss and the kinetics of the processes taking place within the sample. Image of TGA instrument used in our case is shown in Fig. 2.5(b).

TGA is often combined with other analytical techniques like differential scanning calorimetry (DSC) and mass spectrometry (MS) to get more information about the sample's behavior during heating. Applications of TGA include studying polymers, pharmaceuticals, ceramics and other materials. It is a valuable tool for characterizing the thermal properties of the materials and understanding their behavior under different temperature conditions.

Crucibles: Typically made of the materials like alumina or platinum.

Balances: High-precision balance to measure small changes in mass.

Heating Systems: Furnaces or ovens with controlled temperature programs.

Gas Atmosphere Control: Instruments often operate under controlled atmospheres (e.g., N_2) to prevent unwanted reactions.

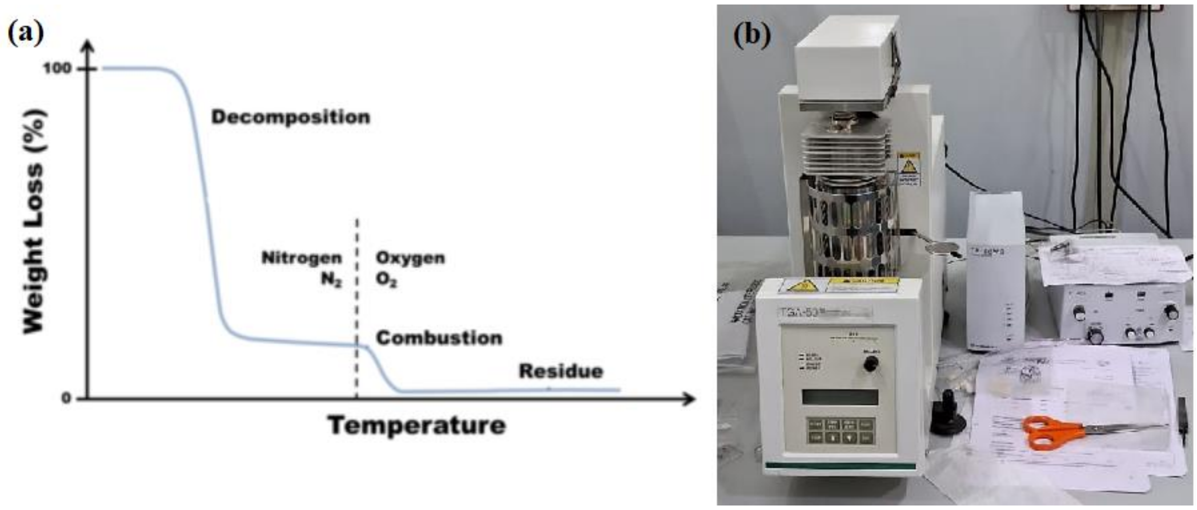

Fig. 2.5 (a) Representation of TGA curve, (b) Image of TGA instrument

2.4.4 Differential Scanning Calorimetry (DSC)

The thermal properties of various materials can be studied using differential scanning calorimetry. Differential scanning calorimetry (DSC) involves measuring the heat difference required to raise the temperature of both a sample and a reference material simultaneously, while varying the temperature. In general, the temperature program is structured to ensure a linear increase in the sample holder's temperature over time and reference sample should be of well-defined heat capacity over operating temperature for DSC measurement. DSC provides information about thermal transition in the materials. The type of reaction occurring (whether endothermic or exothermic) can be determined with the measurement of amount of heat released or absorbed during cooling or heating process in the material using DSC analysis. In this technique, there are two identical sample holders out of which one holds testing sample in a sealed aluminum pan and other one is empty which is used as reference. The temperature of these two sample holders is measured using two identical platinum resistance thermistors. Image of DSC instrument used is shown in Fig. 2.6(b).

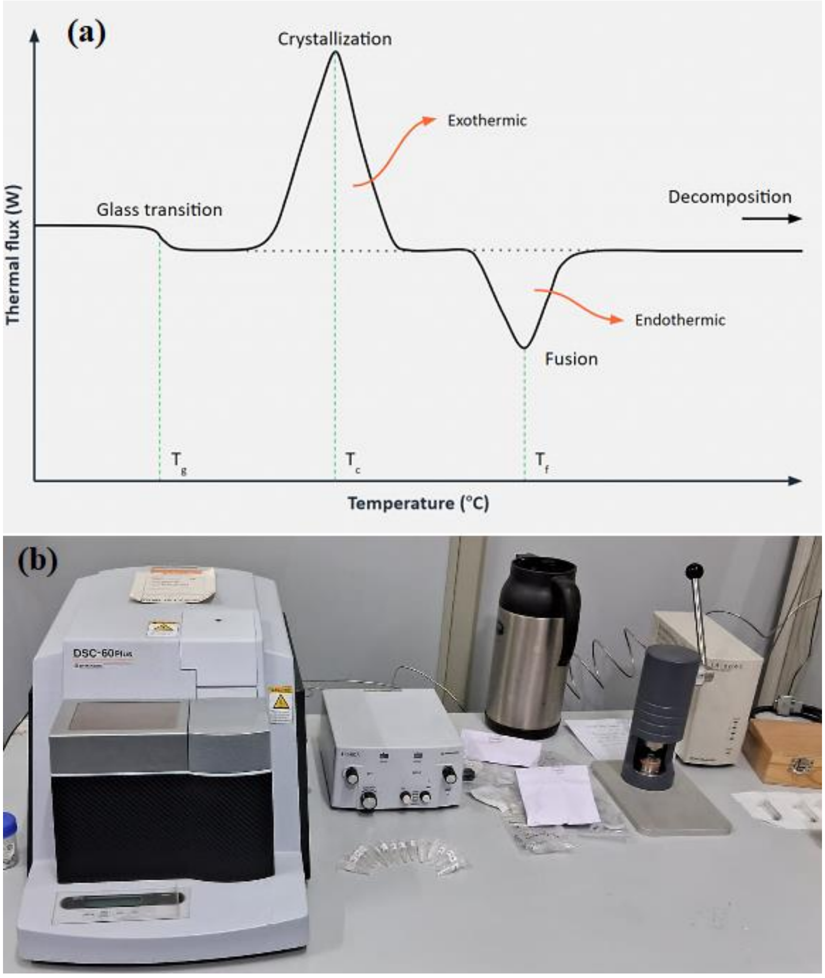

Fig. 2.6(a) Representation of DSC curve, (b) Image of DSC instrument

2.4.5 Field Emission Scanning Electron Microscopy (FESEM)

FESEM stands for Field Emission Scanning Electron Microscopy, which is a powerful technique used for high-resolution imaging of surfaces at the nanoscale. It is an advanced form of scanning electron microscopy (SEM) that utilizes a field emission electron source to achieve extremely fine spatial resolution. Here are some key features and aspects of FESEM analysis:

Unlike conventional SEM, which typically uses a tungsten filament, FESEM employs a field emission electron source. This source produces electrons by the phenomenon of field emission, allowing for a smaller electron probe and higher resolution imaging. FESEM provides higher resolution compared to traditional SEM. It can achieve sub-nanometer resolution, making it suitable for studying fine surface details and structures at the nanoscale. FESEM can achieve high magnifications, allowing researchers to observe specimens in great detail. Magnifications in FESEM typically range from a few times to several hundred thousand times. FESEM is particularly useful for imaging conductive and non-conductive samples. Some FESEM instruments are equipped with detectors that can capture secondary electrons, backscattered electrons, and other signals, providing information about the sample's surface composition and topography. FESEM typically has a greater depth of field compared to traditional SEM, allowing for a larger portion of the sample to be in focus simultaneously. Sample preparation for FESEM analysis involves coating non-conductive samples with a thin layer of conductive material (such as gold or carbon) to prevent charging effects during imaging. Conductive samples may not require coating.

The electron beam is focused on the sample surface. Interaction of the electrons with the sample results in the emission of secondary electrons and backscattered electrons. Detectors capture these emitted electrons, and the signals are processed to create images.The images produced can provide information about the surface morphology, composition, and topography of the sample at a very high resolution.

FESEM is employed to investigate the surface morphology, particle size and distribution, and other structural features of a wide range of materials. Some FESEM systems are equipped with an Energy Dispersive X-ray Spectroscopy (EDS) attachment, allowing for elemental analysis of the sample. This provides information about the chemical composition of the imaged areas.

In summary, FESEM is a valuable tool for researchers and scientists studying materials at the nanoscale. Its high resolution, versatility, and compatibility with various sample types make it an essential instrument in many scientific laboratories and research facilities. FESEM analysis is a powerful tool for researchers and scientists to explore the nanoscale world and obtain detailed information about the surface properties of diverse materials. Interaction of electron beam with sample in FESEM instrument and Image of FESEM instrument is shown in Fig. 2.7(a) and Fig. 2.7(b) respectively.

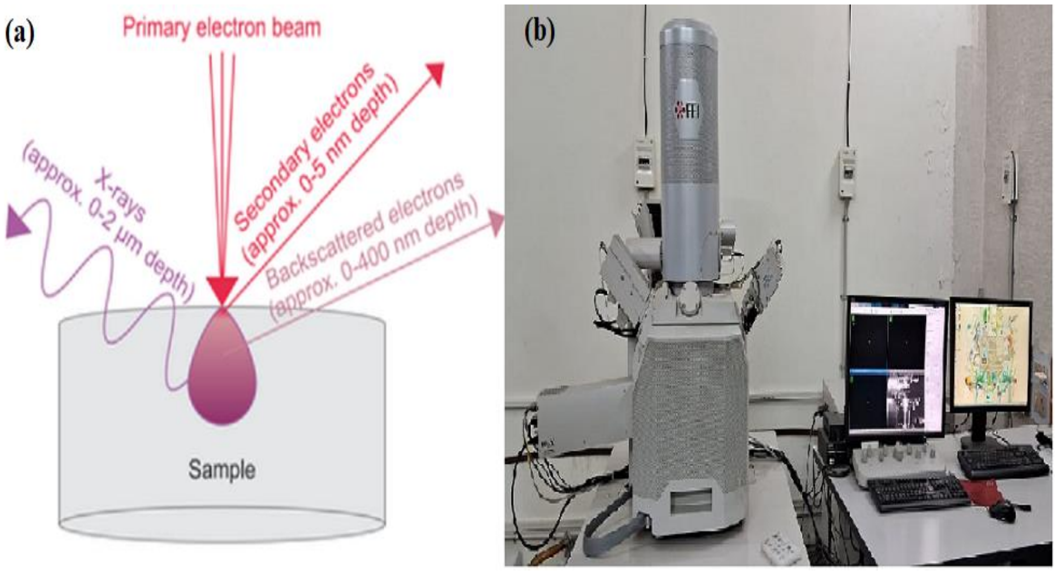

Fig. 2.7 (a) Interaction of electron beam with sample in FESEM, (b) Image of FESEM instrument

2.4.6 Impedance Spectroscopy

Impedance spectroscopy is employed for investigating the electrical characteristics of materials, particularly within electrochemical systems. This method involves assessing a material's impedance across varying frequencies. Impedance, in this context, quantifies the resistance a circuit exhibits to the passage of alternating current (AC). In impedance spectroscopy, a small amplitude AC signal is applied to a material, and the resulting voltage response is analyzed. By varying the frequency of the AC signal, information about the material's electrical properties can be obtained. This technique is commonly used in various fields, including electrochemistry, materials science, and biology. In electrochemistry, impedance spectroscopy is used to study the electrical behavior of electrochemical systems such as batteries, fuel cells, and sensors. It can provide information about processes occurring at the electrode-electrolyte interface, such as charge transfer, ion diffusion, and capacitance. Dielectric measurements are crucial in various fields, including materials science, electronics, telecommunications, and biology.

Dielectric constant is a dimensionless quantity, and it provides information about how much a material can be polarized by an applied electric field. Dielectric loss, also known as tan delta (tanδ), is a measure of the energy dissipation in a dielectric material when subjected to an alternating electric field. It is often expressed as the tangent of the phase angle difference between the voltage and current waveforms in an AC circuit. High dielectric loss indicates that a material absorbs more energy and is less efficient for certain applications, such as in capacitors.

For studying dielectric properties, the capacitance of a capacitor containing the material as a dielectric is measured with varying frequency and temperature and thus dielectric constant and dielectric loss can be obtained with the help of AGILANT software installed in the attached desktop. The sample is inserted between two electrodes, and the capacitance is determined using appropriate instrumentation. Dielectric loss can also be measured using impedance analyzers. The phase angle between the applied voltage and current is measured and tan delta is calculated. Image of dielectric property measurement setup is shown in Fig. 2.8(b).

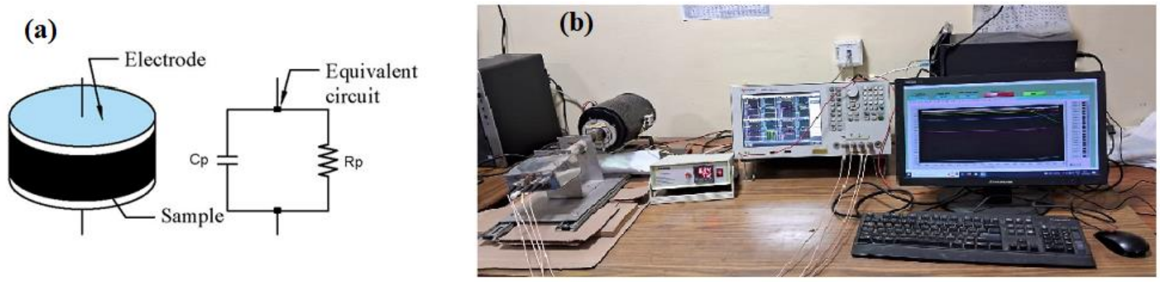

Fig. 2.8 (a) Basic circuit diagram of Impedance spectroscopy, (b) Image of instrument for dielectric property measurement

2.4.7 P-E hysteresis loop Analysis

The measurement of the polarization-electric field (P-E) hysteresis loop is a common technique used to characterize the ferroelectric properties of materials. Ferroelectric materials exhibit a spontaneous electric polarization that can be switched by applied external electric field. Here is a general outline of the process for measuring the P-E hysteresis loop:

Start with the ferroelectric material in its initial, poled state. Apply a small electric field to ensure the material is in a uniform polarization state. Apply an increasing electric field to the material, and record the corresponding polarization values. This is typically done by sweeping the electric field from negative to positive values. Identify the point at which the polarization starts to switch direction. This is known as the coercive field or switching field. Continue increasing the electric field until you reach a maximum value. Then, reverse the electric field direction and record the polarization values as you decrease the electric field. Plot the polarization as a function of the electric field. The resulting graph is the P-E hysteresis loop, which typically forms a closed loop due to the ferroelectric nature of the material. Analyze the hysteresis loop to extract important parameters such as remnant polarization, coercive field, and saturation polarization.

Fig. 2.9(a) represents Sawyer-Tower circuit for measurement of ferroelectric polarization. In Sawyer-Tower circuit, a sample ferroelectric capacitor material is associated with a reference capacitor. The polarization P can be calculated using formula $P= Q/A= C*V/A$, where Q is the charge on the capacitor which is same on both capacitors as they are connected in series combination, A is area of sample electrode and V is the voltage across the reference capacitor which is directly connected with oscilloscope. P-E hysteresis loop analysis was performed using Radiant Technologies' Precision Premier-II ferroelectric tester at various frequencies and sinusoidal ac voltage that gives coercive field and leftover polarization. Sawyer-Tower circuit for ferroelectric polarization measurement and Image of PE hysteresis loop analysis setup is shown in Fig. 2.9.

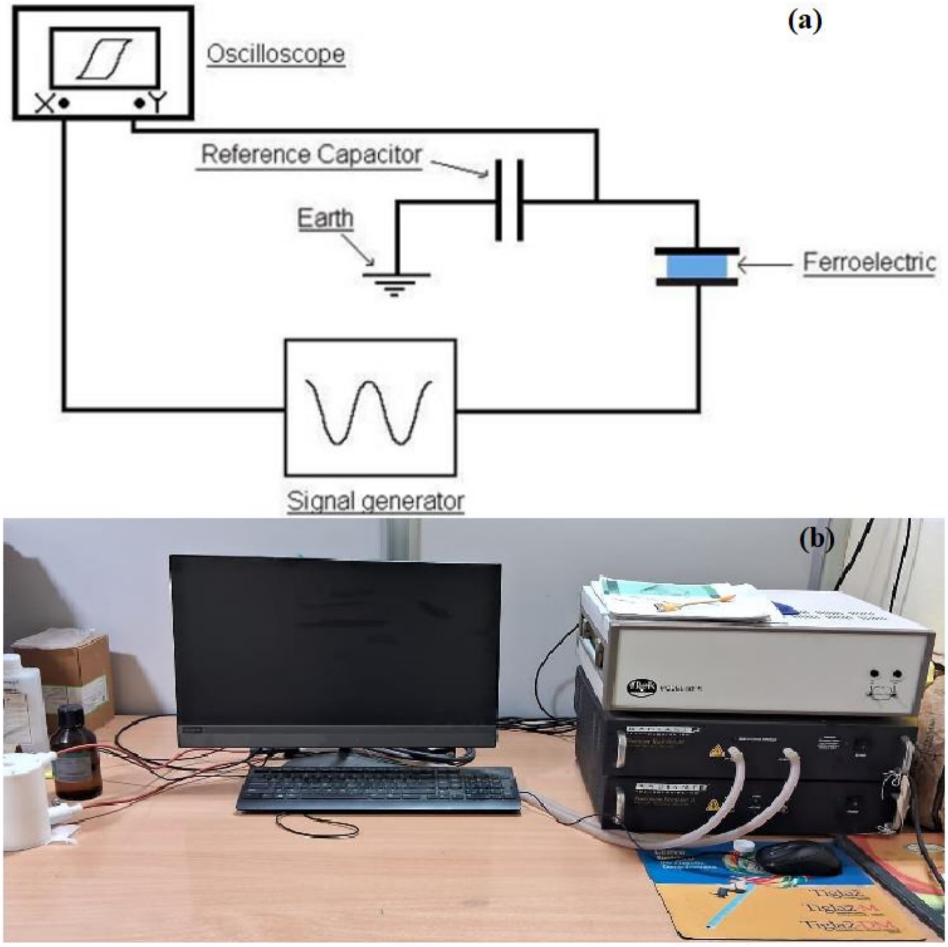

Fig. 2.9 (a) Sawyer-Tower circuit for ferroelectric polarization measurement, (b) Image of PE hysteresis loop analysis instrument

2.4.8 Breakdown strength test set up

Dielectric breakdown strength also known as dielectric strength, is a property of dielectric materials that measures their ability to withstand electrical stress without experiencing electrical breakdown. It is the maximum electric field that a dielectric material can withstand before electrical breakdown occurs, leading to the formation of an electrical discharge or breakdown. It is typically expressed in terms of volts per unit thickness of the material. The standard unit for dielectric breakdown strength is volts per meter (V/m) or kilovolts per millimeter (kV/mm), depending on the specific application.

The breakdown strength of a dielectric material is influenced by various factors, including the material's composition, purity, temperature, and the rate of voltage application. High-quality dielectric materials with good insulating properties generally exhibit higher breakdown strengths.

It's important to note that dielectric breakdown can be a critical consideration in the design and operation of electrical systems, especially in applications such as insulating materials for electrical cables, capacitors, and insulators. The dielectric breakdown strength of a material is a crucial parameter in understanding its electrical insulating properties. This breakdown can lead to the formation of an electrical discharge, such as a spark or arc. Here is the basic step to measure the dielectric breakdown strength of a dielectric material:

Prepare a representative sample of the dielectric material. The sample should be of a specific shape and size, depending on the testing standards or the requirements of the experiment. Set up a test apparatus that allows you to apply a gradually increasing electric field to the dielectric material. This apparatus typically includes two electrodes between which the dielectric is placed. Choose an appropriate electrode configuration. The most common configurations are parallel plates or concentric cylinders, depending on the shape of the sample and the testing standards. Calibrate the measurement system to ensure accurate and reliable results. This may involve checking the accuracy of the voltage and current measuring instruments. Apply a gradually increasing voltage across the electrodes. This can be done at a constant rate until the dielectric breakdown occurs. Monitor the sample for any signs of breakdown, such as the initiation of sparks, flashes, or a sudden increase in current flow. Record the voltage at which breakdown occurs. Analyze the data obtained during the test. Perform multiple tests on different samples to ensure the reliability of the results. The dielectric breakdown strength can vary between samples. The frequency of the AC signal can also impact the breakdown characteristics, so the testing conditions should be specified in accordance with the application requirements.

The dielectric breakdown strength of the PVDF based nanocomposites were measured using AC high voltage (HV) test setup manufactured by Neo tele-Tronix Pvt. Ltd. Kolkata, India (NPTL). HV transformer is the main component in this test setup with control and measuring circuits. In order to achieve an accurate reading, a capacitive high voltage potential divider which is outfitted with a low voltage arm may be attached directly. Image of the instrument used for measuring dielectric breakdown strength is shown in Fig. 2.10.

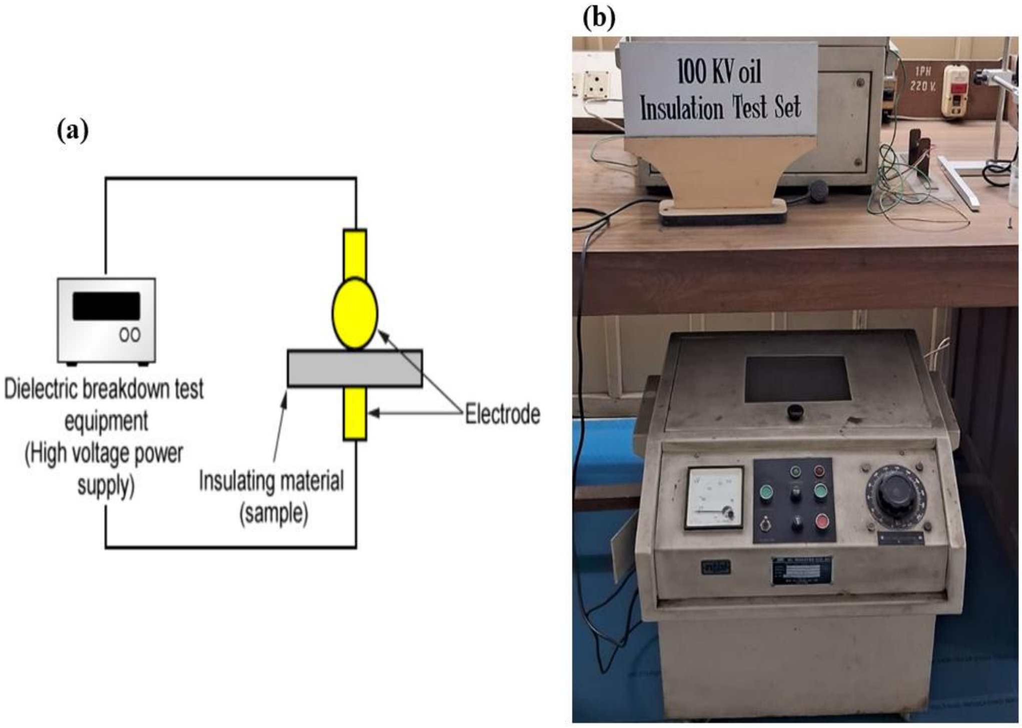

Fig. 2.10 (a) Circuit diagram for dielectric breakdown measurement process, (b) Image of breakdown strength test setup

2.4.9 Atomic Force Microscopy

Atomic Force Microscopy (AFM) serves as a potent imaging method employed in nanoscale investigations for observing and analyzing the surface topography of materials at atomic and molecular scales. This technique generates detailed three-dimensional images by maneuvering a sharp probe (a cantilever equipped with a pointed tip) across the surface of the sample. The heart of AFM is a sharp tip that is usually made up of silicon and attached with a flexible cantilever. The cantilever is a flexible beam that oscillates near its natural frequency. The probe is situated in close proximity to the sample surface, typically within a few nanometers. As the probe nears the sample surface, various forces, including van der Waals forces, electrostatic forces, and chemical bonding forces, become active. These interactions result in the deflection of the cantilever, and this deflection is captured by recording the movement of a laser beam focused on the back of the cantilever. The reflected light is captured by a photodetector and changes in the deflection are translated into a signal. AFM provides exceptionally high lateral and vertical resolution, allowing researchers to visualize features as small as individual atoms. It can be operated in various environments, such as air, liquid, or vacuum. AFM can operate in different modes, such as contact mode (tip constantly in contact with the sample), tapping mode (tip tapping on the sample surface), and non-contact mode (tip intermittently tapping the surface without direct contact). Different modes are chosen based on the specific requirements of the experiment and the type of sample being studied. AFM provides high lateral (horizontal) and vertical resolution, often on the order of nanometers or even sub-nanometers. This makes it a valuable tool for imaging and characterizing materials at the atomic and molecular levels. Applications of AFM include studying the topography of surfaces, measuring mechanical properties of materials, and investigating biological specimens. It is a versatile tool that has contributed significantly to our understanding of nanoscale phenomena. The AFM operates in a feedback mode, where the position of the tip is continuously adjusted to maintain a constant interaction force with the sample surface. This is achieved by monitoring the deflection of the cantilever. A cantilever is exposed to a laser beam directed towards its rear, and a position-sensitive photodetector captures the reflected beam. As the cantilever deflects due to the interaction forces with the sample, the position of the reflected beam changes. The feedback system adjusts the height of the tip to keep a constant force between the tip and the sample. This results in a topographical map of the sample surface. The sample is mounted on a piezoelectric scanner, allowing precise movement in the x, y, and z directions. The tip is raster-scanned across the sample surface, collecting height information at each point. Block diagram and Image of AFM instrument is shown in Fig. 2.11.

In summary, AFM enables high-resolution imaging by sensing the interaction forces between the tip and the sample surface. This technique has found applications in various fields, such as materials science, biology, and nanotechnology, providing valuable insights into surface morphology and properties at the nanoscale.

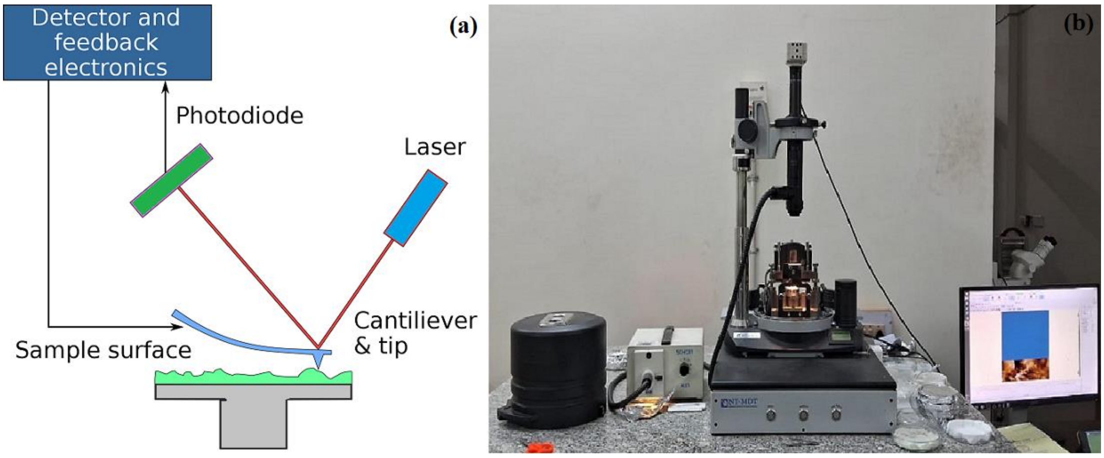

Fig. 2.11 (a) Block diagram of AFM instrument, (b) Image of AFM instrument

2.4.10 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a method that focuses on the surface of materials to examine their chemical composition. This technique offers insights into the elemental composition, chemical state, and electronic state of the elements found on a sample's surface. A standard XPS setup comprises an X-ray source, typically utilizing Al Kα or Mg Kα X-rays, along with an electron analyzer and a detector. To avoid interference from air molecules, the sample is positioned in a vacuum chamber. X-rays are directed onto the sample surface, leading to the ejection of photoelectrons from the atoms in the sample. These photoelectrons are then accelerated and focused towards an electron analyzer. The energy and intensity of the emitted electrons are measured, providing information about the binding energies of the electrons. The binding energy of the photoelectrons is characteristic of the specific element and its chemical state in the sample. Here is a brief overview of the working principle of XPS:

XPS begins with the generation of X-rays. Typically, a monochromatic X-ray source, such as an aluminum or magnesium anode, is used. These X-rays have sufficient energy to penetrate the surface layers of a material. The X-rays are directed onto the sample surface. When X-rays interact with the sample, they can eject inner-shell electrons from the atoms of the material. The ejected electrons are referred to as photoelectrons. The process by which these electrons are emitted is known as the photoelectric effect. According to the photoelectric effect, X-rays can knock out inner-shell electrons from atoms. The kinetic energy of the emitted photoelectrons depends on the energy of the incident X-rays and the binding energy of the electron in its initial state within the atom. The binding energy is specific to each element and can be considered as a characteristic fingerprint. The kinetic energy of the photoelectrons is measured by an electron energy analyzer. This information is then used to determine the binding energy of the electrons. The resulting data is plotted as a spectrum, where the x-axis represents the binding energy and the y-axis represents the intensity of the emitted photoelectrons. Peaks in the spectrum correspond to different elements present in the sample. The detailed analysis of the XPS spectrum allows researchers to not only identify the elements present but also to deduce information about the chemical state of those elements. Different chemical environments (oxidation states, bonding configurations) for an element will result in distinct peaks in the spectrum. It can distinguish between different oxidate states of an element and is particularly useful for studying surfaces and thin films, providing information about the composition and chemical bonding at the atomic level. For XPS analysis, sample must be conductive or be coated with a conductive layer and put in high vacuum condition. Block diagram and Image of XPS instrument is shown in Fig. 2.12.

In summary, XPS utilizes the photoelectric effect to analyze the photoelectrons emitted from a sample when exposed to X-rays, providing valuable information about the surface chemistry of the material under investigation.

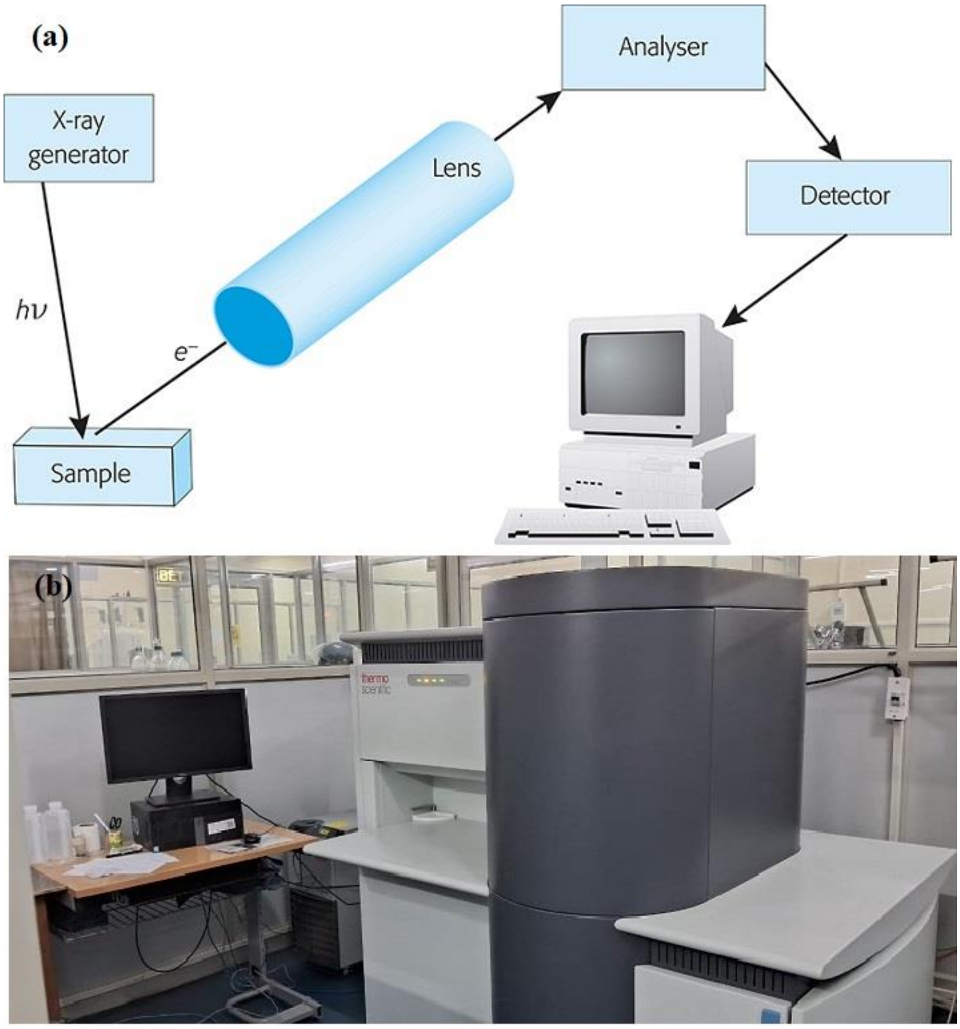

Fig. 2.12 (a) Block diagram of XPS instrument, (b) Image of XPS instrument

2.5 Conclusion

In this chapter, we have discussed the materials used for synthesis of composites and synthesis process of nanoparticles and nanocomposites briefly. The surface modification process of nanoparticles has also been discussed in detail. The characterization techniques used for the synthesized samples have been also discussed. The basic structure of setup, its working principle and image is discussed and shown. In the upcoming chapter, we will discuss about synthesized materials with its properties.