Chapter- 2

Materials and Methods

2.1 General Sample Preparation Methods

Accuracy and quality of result depends upon purity of reactant and the method adopted for preparation of sample. Under this title different methods of sample preparation have been discussed in brief.

2.1.1 Sol-gel method

In sol-gel method the materials are obtained from solution via gelation. The high homogeneity of the constituent elements and the mild processing condition of the sol-gel synthesis such as moderate preparation temperatures make it possible to obtain unique materials not accessible with other. Sol-gel method has been used commercially since 1930s, but the real take off was not until 1970, when it was shown that gel monoliths could be transformed with retained shapes into oxide (Yoldas, 1975), (Yamaneet al., 1978) and that the use of alkoxide precursors allow for low sintering temperature (Mazdiyasni et al., 1969), (Smith II et al., 1970) although monoliths have turned out the least important of the many possibilities of sol-gel synthesis. Other aspects have attracted a continuously growing interest. Sol-gel process is a versatile progression for making the ceramics materials. In general, the sol-gel involves the transition of a system from a liquid solution (mostly colloidal) into a solid gel phase. Applying the sol-gel process it is possible to manufacture ceramic materials in a wide variety of forms. Ultra-fine powders, thin film coatings, micro process in organic membrane and extremely porous aero-gel materials. The starting materials used in the preparation of the solution are usually inorganic metal, salts and metal organic compounds. In
the typical sol-gel process the precursors are subjected to a sequence of hydrolysis and polymerization reaction to formulate a colloidal suspension or a sol. Further processing of the sol empowers one to create ceramic materials in different forms. Further drying and heat treatment the gel is renewed into dense particles. The sol-gel method also has other potential benefits over other traditional processing techniques, one can gain better homogeneities lower processing temperature (Brinker et al., 1990).

2.1.2 Co-precipitation method

(Patnaik, 2004) carried out precipitation of compounds which were normally soluble under employable conditions of co-precipitation. Analogously, in medicine, co precipitation is specifically the precipitation of a free “antigen along with an antigen-antibody complex”.

Co-precipitation is an important issue for synthesis of samples for research purposes and chemical analysis. In gravimetric analysis, which consists on precipitating the analyte and calculating its mass to regulate its concentration or purity, CPT is a problem because undesired impurities often co precipitate with the analyte, resulting in excess mass. This problem can often be mitigated by "digestion" or by re-dissolving the sample and precipitating it again (Harvey, 2000). This method is very much suitable for preparation of micro and nano particles. Main steps are as under:
On the other hand, in the analysis of dopant elements, as is often the case in radiochemistry, co precipitation is often the only way of separating an element. Since the trace element is too dilute (mostly less than a part per trillion) to precipitate by conventional technique, it is typically CPT with a carrier, a substance that has a similar crystalline structure that can incorporate the desired element. An example is the separation of francium from other radioactive elements by CPT it with cesium salts such as cesium perchlorate. Otto Hahn is known for promoting the use of CPT in radiochemistry.

There are three main mechanisms of co precipitation:

a) Inclusion,

b) Occlusion, and

c) Adsorption (Harvey, 2000)
(a) Inclusion: An **inclusion** occurs when the impurity occupies a lattice site in the crystal structure of the carrier, resulting in a crystallographic defect; this can happen when the ionic radius and charge of the impurity are similar to those of the carrier.

(b) Occlusion: An **occlusion** occurs when an adsorbed impurity gets physically trapped inside the crystal as it grows. "potentially important to many environmental issues closely related to water resources, including acid mine drainage, radionuclide migration in fouled waste repositories, metal contaminant transport at industrial and defense sites, metal concentrations in aquatic systems, and wastewater treatment technology”.

(c) Adsorption: An adsorbate is an impurity that is weakly bound (adsorbed) to the surface of the precipitate. It is the phenomenon of transport of weakly bound impurity.

Distribution between the precipitate and the solution:

There are two models which can explain the distribution of the tracer compound between the two phases

(i) Doerner-Hoskins law (logarithmic):

\[
\ln \frac{a}{a-x} = \lambda \ln \frac{b}{b-y}
\]

(ii) Berthelot-Nernst law:

\[
\frac{x}{a-x} = D \frac{y}{b-y}
\]

where:

a and b are the initial concentrations of the dopants and intrinsic substance and carrier, respectively;
(a-x) is concentrations of tracer and 
(b-y) is carrier after separation;

x and y are the masses of the tracer and carrier on the precipitate;

D and λ are the distribution coefficients.

For D and λ greater than one, the precipitate is enriched in the tracer. Depending on the CPT system and conditions either λ or D may be constant. The derivation of the Doerner-Hoskins law adopts that there is no exchange of mass between the interior of the precipitating crystals and the solution. When this condition is fulfilled, then the content of the tracer in the crystal becomes heterogeneous. When the Berthelot-Nernst law is applied, the concentration of the tracer in the interior of the crystal is found uniform the crystals become homogeneous. This is the case when diffusion in the interior is possible, as in the case of liquid, initially small crystals are allowed to recrystallize. Here kinetic effects i.e. speed of crystallization and presence of mixing, play an important role.

2.1.3 Solid state reaction method

The solid-state reaction route is the widely used process for the preparation of polycrystalline solids from a mixture of solid starting materials. Solids do not react together at room temperature over normal time scales and it is required to heat them to much higher temperatures, (between the temperature range: 1000 to 1500 °C) in order for the reaction to occur at an appreciable rate. The aspects on which the possibility and rate of a solid state reaction depend are a) reaction conditions, b) structural properties of the reactants, c) surface area of the solids reactants, d) their reactivity and e) the thermodynamic free energy change associated with the reaction (Anthony, 2005).
For the production of perovskite oxides from the oxides, nitrate, carbonate, sulphate, acetate and other metals salt are used. In this method, the solid reactants are heat-treated to produce new solid solution. In the synthesis of manganite’s and double perovskite, there are six main steps:

Flow Chart-2  Steps of solid state route

A solid state reaction is also known as a dry media reaction or a reaction having no solvent, is a chemical reaction in which solvents are not used. A solid-state reaction route, however, permits the reactants to chemically react without the occurrence of a solvent (Anthony et al., 2005).

The advantages of solid state reactions ripple throughout many industries. The specific benefits of the reaction-steps and product isolation, researchers attract towards it. The main
qualities of these reaction method makes better in comparison of other sample preparation techniques as follows;

(a) Solid state reaction is a conditioned reaction where reactants are present as per the requirement of reaction, at the same time it is easy to decide to estimate the transport of ions. The new compositions can be thought and expected result can be obtained.

(b) Solvent is not required- Since solid state reaction is dry reaction, only the precursors required for reaction are needed, this is why any type of solvent is not required.

(c) It is also economic because the elimination of solvents from the list of reactants, means that production cost will less.

(d) With normal reactions, researchers need to remove the residual solvent from the resulting product after a reaction has finished. In this way we can save time also.

(e) Producing materials from a solid state reaction is obtained in its pure form, free of impurity hence researchers feel free from the process of purification method.

(f) Solid state reaction produces single product.

(g) It is also more environmentally friendly.

There are some precautions e.g. availability of ultra-pure reactants, certification of homogeneity, particle size and different steps of sample preparation which can lead the researchers to prepare a sample successfully. Another important factors of successful preparation of sample are fixation of temperature for pre-sintering and sintering. I have prepared all samples and get remarkable result using this technique. The detail study of this technique is described here.
2.1.3.1 Milling

Milling is back bone of solid state route. Milling or grinding both are the synonym, but in research methodology the term milling refers, a special process in which particle size is reduced in controlled environment. It means the milling tools should be in either planetary ball milling or the mortar and pestle made up pure zirconium element (hard material) so that there will be no chance of any impurities. Although the hour of milling is not fixed, it depends upon the particle size of the reactant. It is better to take reactants of lower particle size for better result.

As particle size is reduced by milling, the surface area of the whole reactants increases and it becomes helpful to manage the rate of reaction. However, it has been observed that if milling has been done properly, the sintering time may be minimized and there will be no chance of failure of the synthesis process. The special attention for milling process is: if it is done manually, milling should be continuous. The rotation of pestle should be managed in such a way all the particles remain in motion. Hand milling may prove most successful if following two precautions have been kept in mind:

i. **Spiral/circular motion of pestle:** Spiral and circular motion of the pestle should start from the bottom of the mortar with minimum radius, radius should increase gradually, as and when pestle approaches just below the edge of mortar, the pestle will move towards the bottom. Such process contributes to minimize the particle size of the sample. The centre of the circular spiral motion should be vertical axis of the mortar.

ii. **Elliptical motion of pestle:** Elliptical motion of pestle should be in such a way, the centre of ellipse should be on the mid of wall and the centre will change its location on
mid circumference of the wall of mortar. This process is very much helpful for best churning of the sample.

A complete milling is combination of above two steps. Preferably there should be one complete elliptical motion after minimum three complete spiral- circular motion. Such a milling style makes the sample homogeneous and lowest particle size.

**2.1.3.2 Pre-sintering**

Pre-sintering is defined as the process of Heating to high temperatures in air or oxygen. However, the word calcination is also used to mean a thermal treatment procedure which can be finished in the absence or monitored supply of air or oxygen applied to ores and other solid materials to bring about decomposition. Calciner is a steel made cylindrical vessel that rotates inside a heated furnace on its axis and performs indirect high-temperature treating (550-1150 °C or 1000-2100 °F) within a controlled thermosphere.

The process of calcination derives its name from the Latin calcinare which stands for burning of lime (Mosby-Year Book Inc). Due to its most common application, the putrefaction of calcium carbonate to calcium oxide and carbon dioxide, in order to create cement. The product of calcination is usually regarded as "calcine", irrespective of the actual minerals undergoing thermal treatment. Calcination is carried out in furnaces or reactors of various designs including shaft furnaces, kilns, multiple, and fluidized bed reactors.

In my research work calcinations is being treated as heat treatment before final sintering. This is why, a nomenclature of this step has become popular as pre-sintering.
During this process, carbonates are decomposed into metal oxides and carbon dioxide. All the volatile impurities and gases have been eliminated by this process.

The decision of pre-sintering temperature is based upon physical properties of the sample. Since this process is done below melting point of the samples, so melting point and nature of volatile impurities are kept in mind.

2.1.3.3 Sintering

Sintering is the process of condensing and forming a solid mass of material by heating and/or exerting pressure devoid of melting it to the point of liquefaction. Sintering happens naturally in mineral deposits or as a mechanized process used in the case of metals, ceramics, plastics, and other materials. The process of diffusion of atoms occurs across the boundaries of the particles of matter, resultantly fusion of the particles takes place and process one solid piece. Examples of pressure-generated sintering are the compacting of snowfall to a glacier.

Sintering is effective when the process reduces the porosity and enhances properties such as strength, electrical conductivity, translucency and thermal conductivity; yet, in other cases, it may be useful to increase its strength. During the heating process, atomic diffusion energies powder surface elimination in different stages, starting from the formation of middle stage between powders to final elimination of pores of small diameter at the end of the process. The driving force for densification is due to the change in free energy from the loss in surface area and dropping of the surface free energy by solid-vapor interfaces. It forms fresh but lower-energy solid-solid interfaces with a total reduction in free energy occurring on sintering one micrometer particles a one cal/g decrease. On a minute scale, material transfer is exaggerated by the variation in pressure and differences in free energy across the curled
surface. If the size of the particle is small and its curvature is high, its effects can be very large in magnitude. The change in energy is observed much higher when the radius of curvature is of micron order, which is one of the main reason, ceramic technology is based on the use of fine-particle materials (Maca et al., 2009).

For properties such as strength and conductivity, the bond area in relation to the particle size is the determining factor. The parameters that can be controlled for any given precursors are the temperature and the initial grain size, because the vapor pressure is governed by temperature.

The change in free or chemical potential energy between the neck and the surface of the particle is the source of power for solid-state processes. This energy creates a transmission of material through the fastest means possible. If transfer were to take place from the particle volume or the grain boundary between particles, then there would be reduction in particle size and destruction in pore. The elimination of pore occurs fast for a shake of time with many pores of uniform size and higher porosity at the same time, the boundary diffusion distance is smaller. For the latter portions of the process, boundary and lattice diffusion from the boundary become more important (Maca et al., 2009).

The proper monitoring of temperature is very important for the sintering process, since grain-boundary diffusion and volume diffusion are function of temperature, the size and dissemination of particles of the material and the materials composition. There are two kinds of sintering:

a) sintering with pressure (also known as hot pressing) and
b) Pressureless sintering. It is possible with graded metal-ceramic composites, with a nanoparticle sintering aid and bulk molding technology. An experimental device used for 3D shapes is called hot isostatic pressing.

If a metal powder under certain external conditions may exhibit coalescence then Sintering is static, and yet relapses to its normal behavior when such conditions are impassive. It has been observed generally that the density of a collection of grains increases as material drifts into voids, causing a loss in overall volume. Mass movements that occur during sintering is main cause of reduction of total porosity by repacking. It is further followed by material transport due to evaporation and condensation from diffusion. In the final stages, movement of metal atoms along crystal boundaries towards the walls of internal pores, reorganizing mass from the internal bulk of the object and polishing the diameter of pore walls. Surface tension is the driving force for this movement.

Under pressureless sintering, three different heating schedules can be followed:

(a) Constant-rate of heating (CRH),

(b) Rate-controlled sintering (RCS) and

(c) Two-step sintering (TSS).

The microstructure and grain size and crystal arrangement of the ceramics guided by the material and method used (Maca, et al., 2005).

Constant-rate of heating (CRH), is also recognized as temperature-controlled sintering, involves heating the green compact at a constant rate up to the sintering temperature. Optimization of sintering temperature has been practiced taking zirconia and sintering rate for CRH method. A conclusion has been made that the grain sizes were identical.
when the samples were sintered to the same density. It proves that grain size is a function of specimen density rather than CRH temperature mode.

In rate-controlled sintering (RCS): The open-porosity phase is lower than in the CRH methodas observed by Oghbaei et al. (Oghbaei, 2010). As observation reveals, the relative density in open-porosity phase is lower than 90%, further it should prevent separation of pores from grain boundaries. It has been noticed statistically that RCS did not yield smaller grain sizes than CRH particularly for alumina, zirconia, and ceria samples (Maca et al., 2005).

Two-step sintering (TSS): In TSS the process of sintering has been done in two stages. The first sintering temperature should guarantee a relative density higher than 75% of theoretical sample density as well as this is proven helpful to eliminate some oxides and volatile impurities, if any how remaining in the sample. This will remove supercritical pores from the samples. The sample is allowed to cool down till room temperature. Preferably the temperature programming for cooling has not done. After that the second sintering temperature is decided as per physical specification of the sample and the process continued until the densification is completed. Grains of cubic zirconia and cubic strontium titanate are considerably refined by TSS compared to CRH. However, the grain size changes in other ceramic ingredients, like tetragonal zirconia and hexagonal alumina, were not statistically significant (Maca et al., 2005).

In microwave sintering, heat is produced internally and it approaches to the surface level of the material, rather than via radiative heat transfer from an external heat source. Other paybacks of microwave sintering are a better heat diffusion, shorter time needed to reach the sintering temperature, less heat energy required and enhancements in the product properties (Oghbaei et al., 2010).
As microwaves can only pierce a short distance inside the materials with a high conductivity and a high permeability, microwave sintering requires the sample to be delivered in triturates with a particle size around the penetration depth of microwaves in the particular material. It has been observed that the sintering process and solid state side-reactions run several times faster during microwave sintering at the same temperature, which outcomes in different properties for the sintered product (Oghbaei et al., 2010). This technique is acknowledged to be fairly effective in maintaining fine grains/nano sized grains in after first stage sintered bio-ceramics. The examples of such samples are magnesium phosphates and calcium phosphates, which have been synthesized through microwave sintering technique (Babaie et al., 2016).

The sintering of liquid-phase materials includes a fine-grained solid phase to generate the needed capillary pressures proportional to its diameter and the liquid sample concentration must also create the required capillary pressure within range, else the process ends. The vitrification rate is directly dependent upon the pore size, the viscosity and amount of liquid phase present in the sample leading to the viscosity of the complete composition, and the surface tension. Temperature dependence for densification pedals the process because at higher temperatures viscosity decreases liquid content. Therefore, when changes to the composition and processing are made, it will influence the vitrification process.

Sintering occurs by diffusion of atoms through the microstructure of the sample. This diffusion is caused by an ingredient of chemical potential – atoms move from an area of higher chemical potential to an area of lower chemical potential (Smallman et al., 2010). The six common sintering mechanisms are:

- Surface diffusion – It is defined as diffusion of atoms along the surface of a particle
- Vapor transport – Evaporation of atoms precursors which condense on a different surface
- Lattice diffusion from surface – atoms of the sample diffuse through lattice
- Lattice diffusion from grain boundary – atoms from grain boundary diffuse through lattice of the microstructure
- Grain boundary diffusion
- Plastic deformation – displacement motion causes flow of matter

2.1.3.4 Sintering temperatures

As discussed earlier, the aim of sintering is not just melt the solid solution and expect the reaction might be over after some time. This is fully controlled way of heating, in which each atom has sufficient time to interact with the neighbor atom. Although there is no fixed formula to decide the sintering temperature, whenever we decide the temperature, keep some important points in mind:

(a) Melting point of the sample
(b) Hardness of the constituents
(c) Position of the constituents in reactivity series
(d) Atomic –molecular size of the reactants
(e) Ionization potentials of atoms used in the compound.

Since the solid solution is heated below melting points of the constituents so there is no chance of formation of dense paste of the sample, and increase the mobility but several important phenomena occur, already discussed in previous title, so at the time of sintering we do not supply heat suddenly. In practice, heat is raised at the rate of 10 °C per minute and
when optimum temperature is reached, it is fixed for 2 to 4 hrs. as per requirement of the sample.

2.2 Spectroscopy and measuring instrumentation

For the characterization of samples, some spectroscopic techniques have been employed. Under this title a brief introduction, working and way of providing result have been discussed. Specification and brand of the spectroscopy used in all chapters are not same so these are embedded in the body of chapter; where the devices have been used. Further investigations have been done using impedance analyzer and perturbed angular correlation technique.

2.2.1 Spectroscopy

2.2.1.1 X-ray diffractometer (XRD)

The electromagnetic radiations of short wavelength range from $\sim 10^{-5}$ Å to 100 Å the X-rays are produced by transitions of high to moderate energy electrons of inner orbitals of atoms. X-ray fluorescence, X-ray crystallography and X-ray radiography are the three main applications of X-rays. Long range ordering in crystal lattice is characterized using XRD. X-rays can be assumed to be waves of electromagnetic radiation while crystals as regular arrays of atoms. Interaction among electric vector of X-radiation and electrons of the atoms in the crystals through which the x-radiation passes causes scattering. When these x-rays are
scattered through this ordered environment in a crystal, both the constructive and destructive interference take place from the scattered rays. This happens because of the similar scattered centers which are of the order of the magnitude as the wavelength of radiation. This is how the diffraction results. Thus, what makes the requirements for diffraction of x-rays is; (a) the wavelength of the radiation has roughly to be the same as the spacing between the layers of atoms and (b) there must be spatial distribution of scattering centers distributed in regular way. In fact, what causes the beam of x-rays to diffract into many specific directions are the crystalline atoms in the molecular structure of a crystal. A three-dimensional picture of the density of electrons within the crystal can be produced by a crystallographer from angles and intensities of diffracted beams from x-ray diffractometer.

2.2.1.1 Single-crystal x-ray diffraction

In single crystal x-ray diffraction measurements, goniometer is employed for crystal mounting. One can make it for the goniometer to be positioned at selected crystal orientations. Monochromatic beam of x-rays is focused finely to illuminate the crystal in order to produce diffraction pattern by virtue of reflections from regularly spaced points. Combined with inputs from chemical data already known for the sample, the mathematical model of Fourier Transforms is employed to transform 2-dimensional images, as obtained above at different orientations, to 3-dimensional configuration of electron density within the crystal.

One can make use of x-ray crystallography for several other means of obtaining information on atomic structures. Fourier transform may be employed to interpret diffraction patterns on scattering of electrons or neutrons.
Small angle x-ray scatterings, powder or fiber diffractions are also various other methods to obtain partial information if single crystals could not be possible of sufficient size.

2.2.1.1.2 X-ray powder diffraction

If the material under investigation is only available in the form of nanocrystalline powders or suffers from poor crystallinity, the methods of electron crystallography can be applied for determining the atomic structure.

For all above mentioned x-ray diffraction methods, the scattering is elastic; the scattered x-rays have the same wavelength as the incoming x-ray. By contrast, inelastic x-ray scattering methods are useful in studying excitations of the sample, rather than the distribution of its atoms.

Further, constructive interference requires for the optical path difference between two waves to be an integral multiple of wavelengths. Secondary spherical waves are produced from an electron when x-ray strikes the electron, as an elastic scattering phenomenon. Though, in most directions the waves cancel through destructive interference but in a few specific directions they add constructively as per Bragg's law:

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

with \(d\) as spacing between the diffracting planes, \(\theta\) an angle of incidence of x-ray beam, \(n\) any integer and \(\lambda\) the beam wavelength. The spectrum will contain the diffraction intensity verses the diffraction angle. The composition of samples can also be obtained through application of computer software by comparing results so obtained to analytical standard information available. The long range ordering of the sample determines the intensity of diffracted peaks. The uniformity of the crystal lattice determines the sharpness and intensity
of the peaks. Grimaldi (Grimaldi, 1665) predicted that a wave that impinges on regular pattern of scatterers causes diffraction to happen and for significant diffraction, the spacings between the scatterers and the impinging wave length should be of similar sizes.

2.2.1.2 **Scanning electron microscopy (SEM)**

Scanning electron microscope (SEM) is an electron microscope used to develop sample images by scanning with focused beam of electrons. The interaction of electrons with sample atoms generates signals which contain information on surface topography and morphology of the sample. Raster scan patterns scans the electron beam combined with unique signal to produce an image. The SEM can have resolution as better as 1 nm. Specimens can be observed in

(a) high vacuum or low vacuum,

(b) wet conditions and

(c) at an extensive range of cryogenic or elevated temperatures.

The most common SEM mode is the detection of secondary electrons emitted by atoms after excitation of electron beam. The number of secondary electrons that can be sensed depends, among other things, on the angle at which beam meets troposphere of specimen i.e. on specimen topography. By focusing the electron beam at sample surface and collecting the secondary electrons an image can be transformed in digital form and be available on computer screen. The types of signals produced by an SEM include

(a) secondary electrons (SE),

(b) reflected or back-scattered electrons (BSE),
(c) photons of characteristic X-rays and light (cathode luminescence).

(d) absorbed current (specimen current) and

(e) Transmitted electrons.

(a) Secondary electron detectors are standard equipment in all SEM. The signals result from interactions of the electron beam with atoms at various depths within the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the secondary electrons are emitted from very close to the specimen surface. Consequently, SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size.

(b) Back-scattered electrons (BSE) are electrons beam that are received on reflection from the sample due to elastic scattering. They appear from deeper locations within the specimen and subsequently the resolution of BSE images is normally poorer than SE images. However, BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays, because the intensity of the BSE signal is directly related to the atomic number of the specimen. BSE responses are changed inti images, which can provide information about the dissemination of different elements in the sample. Due to these reasons, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameters, which would otherwise be difficult or impossible to identify in secondary electron images in biological specimens.

(c) Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher-energy electron to fill the shell and release
energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Due to being highest melting point and lowest vapor pressure of all metals, tungsten metal is generally used in thermionic electron, thereby allowing it to be electrically heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride (LaB₆) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is advanced or field emission guns (FEG), which may be of the cold-cathode type using tungsten single crystal emitters or the thermally supported Schottky type, that use emitters of zirconium oxide.

(d) In SEM, the electron beam, which typically has an energy ranging from 0.2 keV to 40 keV, is conversed by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam is allowed to pass through pairs of scanning coils or deflector plates in the electron column, and ultimately in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a selected rectangular area of the sample surface.

When the primary electron beam interacts with the sample, the electrons lose their energy by frequent random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which scan length from less than 100 nm to approximately 5 μm into the surface. The size of the interaction volume is function of the electron's landing energy, the total number of electrons present in the atom of the specimen and the specimen's density. The energy exchange between the
electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation. e) Transmitted electrons: Some fraction of electron transmits through the inner depth of the atomic configuration of the sample. Study of these transmitted electron energy, surface as well as inner structure can be studied.

In my present work study have been done using energy of backscattered electrons (BSE). It consists of high-energy electrons originating in the electron beam that are reflected or back-scattered out of the specimen interaction volume by elastic scattering interactions with specimen atoms. Since heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), and thus appear brighter in the image, BSE are used to detect contrast between areas with different chemical compositions.

Fig.2.1 Backscattered electron microscopy
The Everhart-Thornley detector, which is normally positioned to one side of the specimen, is inefficient for the detection of backscattered electrons because few such electrons are emitted in the solid angle subtended by the detector, and because the positively biased detection grid has little ability to attract the higher energy BSE. Dedicated backscattered electron detectors are positioned above the sample in a "doughnut" type arrangement, concentric with the electron beam, maximizing the solid angle of collection. BSE detectors are usually either of scintillator or of semiconductor types. When all parts of the detector are used to collect electrons symmetrically about the beam, atomic number contrast is produced. However, strong topographic contrast is produced by collecting back-scattered electrons from one side above the specimen using an asymmetrical, directional BSE detector; the resulting contrast appears as illumination of the topography from that side. Semiconductor detectors can be made in radial segments that can be switched in or out to control the type of contrast produced and its directionality. Backscattered electrons can also be used to form an electron backscatter diffraction (EBSD) image that can be used to determine the crystallographic structure of the specimen.

2.2.1.3 Transmission electron microscopy (TEM)

In transmission electron microscopy (TEM) a beam of electrons is transmitted through ultra-thin specimen. The beam of electrons interacts with specimen while passing through it and makes an image which can be magnified and focused on some imaging device, like fluorescent screen or detected through sensors such as in a CCD camera.

The small de Broglie wavelength of electrons enables TEMs to be capable of producing images with significantly larger resolutions than optical microscopes. This empowers the instrument to examine particles as small as column of atoms, i.e., thousands of
times smaller than the smallest resolvable object in a simple electron microscope. TEM is an important tool to analyze small size particles or grains in scientific fields, in physical, chemical and biological sciences. It has also wide application in cancer research, virology, materials science as well as pollution, nanotechnology, and semiconductor research.

At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging.

2.2.1.4 **Energy-dispersive x-ray spectroscopy (EDS)**

Energy-dispersive X-ray spectroscopy (EDS) is an investigative technique useful for elemental analysis or chemical characterization of a sample. It basically depends on interaction of some source of x-ray excitation and a variety of sample (Corbari et al., 2008).

The fundamental principle of characterization capabilities is based upon the fact that each element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum (Goldstein, 2003). A high-energy beam of charged particles is used to stimulate the release of characteristic X-rays from a sample, i.e. electrons or protons, or a beam of X-rays, is focused. Normally at rest, an atom within the sample contains electrons in ground state in different energy levels or electron shells attached to the nucleus. The incident beam may stimulate an electron in an inner shell, expelling it from the shell while creating an electron
hole where the electron was existing. An electron having higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be depicted in the form of an X-ray. The number and energy level of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. Goldstein (Goldstein, 2003) suggested that the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDS allows the elemental composition of the sample taken to be measured.

When we use EDS technique to characterize the sample we should keep in mind the foresaid affairs. Accuracy of EDS spectrum can be affected by following factors-

a) Voltage fluctuation at the time of spectroscopy

b) The even polishing of the sample surface

Limitations of the spectroscopy is, i) appearance of some overlapped peaks e.g., Ti K\(_\beta\) and V K\(_\alpha\), Mn K\(_\beta\) and Fe K\(_\alpha\) and ii) The X-ray peaks does not give proper peak informations if the sample is heterogeneous.

### 2.2.1.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a topography-sensitive quantitative spectroscopic technique. With help of this technique, elemental composition at the parts per thousand range, empirical formula, chemical state and electronic state of the elements can be studied. The sample is irradiated by a stimulated beam of X-ray and spectra have been obtained, simultaneously the kinetic energy is measured and number of electrons that escape from the top 0 to 10 nm of the material being analyzed. XPS system works on very high or ultrahigh range of the vacuum (VHV; \(P \sim 10^{-8}\) to UHV; \(P < 10^{-9}\)).
2.2.1.6 Fourier Transform Infrared spectroscopy (FTIR)

The term Fourier transform infrared spectroscopy originates from the fact that a Fourier transformation (a mathematical process) is required to renovate the raw data into the actual spectrum for other uses of this kind of technique. Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of either absorption or emission from sample (solid, liquid or gas). An FTIR spectrometer accumulates high spectral resolution data (Griffiths, 2007) over a wide spectral range.

FTIR is a kind of opto-electronic device which works on the principle of measuring infrared absorption and emission spectra. FTIR spectrometers are commonly used for measurements in the mid and near infrared regions (IR). To achieve mid-IR region, 2–25 µm (5000–400 cm$^{-1}$), the silicon carbide element heated to about 1200 K. The output so obtained is similar to a blackbody radiation. A tungsten-halogen lamp (a higher temperature source) is used for shorter wavelengths of the near-IR, 1–2.5 µm (10000–4000 cm$^{-1}$). The long wavelength output of these is limited to about 5 µm (2000 cm$^{-1}$) by the absorption of the quartz envelope. A mercury discharge lamp gives higher output than a thermal source to be used for the far-IR, especially at wavelengths beyond 50 µm (200 cm$^{-1}$).

The goal of any absorption spectroscopy is to measure how well a sample absorbs light at each wavelength. The most common method to do this, the "dispersive spectroscopy". In this technique, a monochromatic light beam is allowed to incident on the surface of sample, measurement of the absorbed light is done, and it is repeated for each different wavelength. The beam described above is produced by starting with a broadband light source, one containing the full spectrum of wavelengths to be measured. The light glosses into a Michelson interferometer, a certain arrangement of mirrors, one of which is monitored by a
motor. As this mirror moves, each wavelength of light in the beam is frequently blocked and transmitted by the interferometer, due to wave interference. Different wavelengths are modulated at different rates, so that at each moment, the beam coming out of the interferometer has a different spectrum.

Next, the observed beam is modified to contain a different combination of frequencies, giving a second data point. This process is performed frequently and this output is given to a computer, which collects all these data and works backwards to infer what the absorption is at each wavelength.

Griffiths (Griffiths, 2007) suggested three principal advantages for an FT spectrometer compared to a scanning (dispersive) spectrometer:

1. The multiplex or Fellgett's advantage: According to this advantage, the information is collected simultaneously from all available wavelengths which result in higher Signal-to-noise ratio during a known scan-time.

2. The throughput or Jacquinot's advantage: This advantage is in a dispersive instrument. The entrance and exit slits of the monochromator restrict the amount of light that passes through it.

3. The wavelength accuracy or Connes' advantage: The wavelength scale is calibrated by a laser beam of known wavelength that passes through the interferometer. This is much more stable and accurate than in dispersive instruments where the scale depends on the mechanical movement of diffraction gratings. In practice, the accuracy is limited by the divergence of the beam in the interferometer which depends on the resolution.
Another minor advantage is less sensitivity to stray light, that is radiation of one wavelength appearing at another wavelength in the spectrum. In dispersive instruments, this is the result of imperfections in the diffraction gratings and accidental reflections. In FT instruments there is no direct equivalent as the apparent wavelength is calculated by the modulation frequency in the interferometer. This device has been employed to detect and analyze metal oxide bond in my work.

2.2.2 Impedance analyzer

To certify the electric and dielectric properties of sample, it is necessary to measure impedance of through the it. The device used for this purpose is called as an LCR meter. It is a type of electronic test equipment used to measure

i) the inductance (L),

ii) capacitance (C), and

iii) resistance (R) of an electronic component.

In the simpler versions of this instrument the impedance was measured internally and converted for display to the corresponding capacitance or inductance value. Readings should be reasonably accurate if the capacitor or inductor device under test does not have a significant resistive component of impedance. More advanced designs measure true inductance or capacitance, as well as the equivalent series resistance of capacitors and the Q factor of inductive components.

Usually the device under test is subjected to an AC voltage source. The meter measures the voltage across sample and the current through it. From the ratio of these the meter can determine the magnitude of the impedance. The phase angle between the voltage and current
is also measured in more advanced instruments; in combination with the impedance, the equivalent capacitance or inductance, and resistance, across the sample can be calculated and displayed. The meter must assume either a parallel or a series model for these two elements. The most useful assumption:

i) LR measurements have the elements in series (as would be encountered in an inductor coil)

ii) CR measurements have the elements in parallel.

An LCR meter can also be used to judge the inductance variation with respect to the rotor position in permanent magnet machines (however care must be taken as some LCR meters can be damaged by the generated EMF produced by turning the rotor of a permanent-magnet motor).

Handheld LCR meters typically have selectable test frequencies of 100 Hz, 120 Hz, 1 KHz, 10 KHz, and 100 KHz for top end meters. The display resolution and measurement range capability will typically change with test frequency.

Bench top LCR meters typically have selectable test frequencies of more than 100 KHz. They often include options to superimpose a DC voltage or current on the AC measuring signal. Lower end meters offer the possibility to externally supply these DC voltages or currents while higher end devices can supply them internally. In addition, bench top meters allow the usage of special fixtures to measure SMD components, air-core coils or transformers.

For the purpose of dielectric measurement first of all the pellet of the sample has been gold polished and put into sample holder of Agilent precision LCR meter. Capacitance and
resistance matrices and graphical representation have been collected with help of computer soft facility. For study of some samples Wayne Kerr Electronics made impedance measurement device has been also used.

2.2.3 Time differential perturbed angular correlation (TDPAC)

Hamilton (Hamilton, 1940) presented his work related to theory of directional correlation of a gamma-gamma cascade. After seven years, Brady and Deutsch successfully measured such a correlation (Brady et al., 1947). They had to work with Geiger counters that combine low detection efficiency with a very bad time resolution and no energy resolution at all, and it is really amazing that a positive result was obtained with such rather primitive equipment. The experimental conditions improved considerably when scintillation detectors became available. In this way, a new technique to determine spins and parities of nuclear states came in practice which was based on gamma-gamma angular correlation experiments. Later on it was realized that extra nuclear fields may perturb and sometimes completely wipe out the angular correlation (Goertzel, 1946). As a matter of fact, this property allowed the determination of the nuclear g-factor (Goertzel et al., 1951) and of the nuclear quadrupole moment (Schönberg et al., 1953), and offered a tool to investigate solid state properties (Heer et al., 1959).

Several changes made this technique more precise and the first report on a time-differential perturbed angular correlation (TDPAC) measurement was presented Lehmann et al. (Lehmann, 1955). The first PAC experiments were employed to measure hyperfine fields, either magnetic or electric. In these experiments a suitable nuclear probe was introduced into the sample, usually being a chemical compound or a dilute alloy. One of the aims of the experiments of that early period was to collect data in a systematic way on magnetic hyperfine
fields in ferromagnetic materials like iron, cobalt, nickel and gadolinium, and on electric field gradients in chemical compounds and non-cubic metals.

A few years later, point defects in metals had become a fashionable field of applications of the PAC technique. By that time, PAC had evolved into a method that is still widely used to study a large variety of solid state parameters at atomic scale.

The result of Pauli Exclusion Principle suggests that the electrons in an atom are located at different energy levels within the atom. These energy levels are separated by energies of the order of eV. The degeneracy of these levels is lifted due to the spin orbit coupling and the atomic levels are split into different energy levels separated by MeV. This is the fine structure of the atomic levels. The atomic nucleus is not spherically symmetric. The charge-charge interactions between nucleus and electrons can bring nonzero quadrupole terms in their interaction Hamiltonian. This non-zero quadrupole terms produce an electric field gradient (EFG) in the atom. The dipole contributions of current-current interactions between nucleus and the electrons can produce magnetic hyperfine fields inside the crystal thus giving rise to hyperfine structure of an atom.

2.2.3.1 Angular Correlation

When an excited nucleus decays through more than one intermediate state then the emission of second gamma radiation is no longer isotropic in nature rather it depends upon the emission of first γ-radiation. It means γ-radiations are angularly correlated. Angular correlations involve two types:

i. Unperturbed angular correlations
ii. Perturbed angular correlations

2.2.3.1.1 Unperturbed Angular correlation

In unperturbed angular correlation the nucleus goes through a very short lived intermediate state such that nuclear moments in that state cannot interact with the environment and angular correlation will not be disturbed and the initial state with nuclear spin \(|I_i, m_i\rangle\) decays through the emission of a \(\gamma\)-quant \(\gamma_1\) in an interstitial state \(|I_s,m_s\rangle\) and this under emission of a second \(\gamma\)-quant \(\gamma_2\) in the final state or ground state \(|I_f, m_f\rangle\), then the relative probability \(W(\theta)\) of detecting \(\gamma_2\) in the solid angle \(d\Omega\) with the angle \(\theta\) in respect to \(\gamma_1\) is given by:

\[
W(\theta) = \sum A_k P_k(\cos \theta)
\]

Where \(A_k\) is anisotropy parameter and \(P_k(\cos \theta)\) is Legendre polynomial. If the nucleus remains in the intermediate state for a relatively longer time, then the nuclear moments can interact with the environment causing the angular spin vector to process. This alters the directional dependence of the gamma emission thereby causing perturbation in the observed correlation function.

2.2.3.1.2 Perturbed Angular Correlation

If the lifetime of the intermediate state is sufficiently large, of the order of a few nanoseconds, then the nucleus in the intermediate state has sufficient time to interact with the environment (extra-nuclear fields). Then the corresponding relation becomes:

\[
W(\theta) = \sum G_k(t) A_k P_k(\cos \theta)
\]
Figure 2.2 Schematic illustration of a $\gamma$-$\gamma$-cascade

Where $G_k(t)$ is the perturbation factor containing information about the electromagnetic interaction. Both the magnetic and the electric interactions exercise a torque on the angular momentum of the intermediate state which produces a precession of $\vec{I}_s$ around the symmetry axis. Quantum mechanically this means that the interaction can lead to transitions among the $m$-states.

2.2.3.1.2.1 Time integral perturbed angular correlation (TIPAC)

If however, the mean life of the intermediate state of the cascade under investigation is smaller than the resolving time of the coincidence circuit, then the overall attenuation of the correlation coefficients can only be measured. The time integral perturbed angular correlation (TIPAC) function is given as;

$$W(\phi, \alpha) = 1 + \Sigma_k a_k G_k(\alpha) P_k(\cos \phi)$$
G_k (α) being the time integral perturbed attenuation coefficients. The values of attenuation coefficients depend upon the magnitude and nature of interaction between the nuclei in their intermediate state and the environment.

2.2.3.1.2.2 Time differential perturbed angular correlation (TDPAC)

The time differential perturbed angular correlation (TDPAC) between two gamma rays in cascade can be written as:

\[ W(\theta, t) = 1 + \sum_k a_k G_k P_k(\cos \theta), \]

where G_k are the time differential perturbation or attenuation coefficients. For time differential measurements the resolving time of the coincidence circuit should be smaller than the mean life time of the intermediate state. In conjunction with fast electronics, the resolving time of the order of few nano-seconds is possible with the assemblies of small NaI (TI) and/ or plastic scintillation detectors or relatively new scintillation materials like planar LaBr_3(Ce) detectors, as used in the present work.

2.2.3.2 Sample preparation for PAC measurements

The \(^{181}\text{Hf}\) tracer was prepared through neutron activation in reaction \(^{180}\text{Hf} \ (n,\gamma) ^{181}\text{Hf}\) with thermal neutron flux of \(\sim5 \times 10^{13} \text{ n/cm}^2\). The stock solution of \(^{181}\text{Hf}\) tracer with 0.1572 mg/ml hafnium was prepared by dissolving neutron irradiated HfCl_4 in dilute HCl. 300µl of stock \(^{181}\text{Hf}\) solution was taken in 10ml of 3(N) HCl and 7ml of Ti-doped BZT samples (barium zinc titanate and barium zirconium titanate) solution was added to it dropwise resulting in the formation of white lump. It was stirred until the lump was dissolved and a
clear solution was obtained. To this solution, ammonia solution was added dropwise to obtain a white precipitate doped with $^{181}$Hf. The white precipitate was filtered off and washed with water several times. The precipitate was then dried and crushed to have TiO$_2$ matrix doped with $^{181}$Hf. The sample got an activity of 11000 Bq/gm with respect to $^{181}$Hf tracer. The prepared sample was then ready for further examination purposes.

### 2.2.3.3 Geometry used to determine hyperfine parameters

The samples so prepared were placed in sample holder of angular correlation table, specially designed geometry for such purposes and coincidence data was recorded with three planar LaBr$_3$(Ce) detectors as shown in fig.2.1. Source was kept at a distance of 1-2 cm from the detector. The unipolar output from each of the amplifiers with a shaping time of 1 $\mu$s was used for the energy measurement.

![Angular Correlation Table](image)

*Fig. 2.3 Angular Correlation Table*
The signals obtained from the detectors were sent to an electronic circuit called CAMEC as shown in Fig. 2.2, where the signals were refined and used for calculation of PAC parameters.

![CAMEC, an electronic device for refining data](image)

**Fig. 2.4** CAMEC, an electronic device for refining data

The ME spectroscopy can be used to measure interaction frequency and electric field gradient of these effects as well as nuclear magnetic dipole interaction. However, ME measurements are often only practical on crystal that have one of several elements as a measure constituent, that is either Fe and Sn. In addition to it, the ME sensitivity depends on temperature. However, the PAC measurement is independent of temperature, which can be a great advantage for studying phenomenon such as phase transition.

There are many techniques to study the hyperfine interactions, viz; Nuclear Magnetic Resonance (NMR), Mossbauer spectroscopy and Perturbed Angular Correlations (PAC). The PAC technique has its own advantages over other conventional methods. It is hoped that PAC study of the complexes of BZT ceramics, will reveal a valuable interlink of dielectric
properties and electric field gradient. The effect of doping with BZT complexes may be analyzed successfully using PAC technique.

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