CHAPTER 2

EXPERIMENTAL TECHNIQUES FOR THE SYNTHESIS AND CHARACTERIZATION OF NANOMATERIALS

2.1. Introduction:

In order to explore novel physical properties and phenomena and realize potential applications of nanostructures and nanomaterials, the ability to fabricate and process nanomaterials and nanostructures is the first cornerstone in nanotechnology. There exist a number of methods to synthesize the nanomaterials which are categorized in two techniques “top down and bottom up”. Solid state route, ball milling comes in the category of top down approach, while wet chemical routes like sol-gel, co-precipitation, etc. come in the category of bottom up approach. Secondly, characterization of nanomaterials is necessary to analyze their various properties. Therefore, this chapter describes the various methods of synthesis and characterization of nanomaterials. Characterization techniques include XRD, SEM, TEM, EDAX, UV-Visible spectroscopy, FTIR spectroscopy, etc.

2.2. Synthesis of Nanomaterials:

Fabrication of nanomaterials with strict control over size, shape, and crystalline structure has become very important for the applications of nanotechnology in numerous fields including catalysis, medicine, and electronics. Synthesis methods for nanoparticles are typically grouped into two categories: “top-down”
and “bottom-up” approach. The first involves the division of a massive solid into smaller and smaller portions, successively reaching to nanometer size. This approach may involve milling or attrition. The second, “bottom-up”, method of nanoparticle fabrication involves the condensation of atoms or molecular entities in a gas phase or in solution to form the material in the nanometer range. The latter approach is far more popular in the synthesis of nanoparticles owing to several advantages associated with it. Fig. 2.1 shows the general overview of the two approaches. There are many bottom up methods of synthesizing metal oxide nanomaterials, such as hydrothermal, [1, 2] combustion synthesis [3], gas-phase methods [4, 5], microwave synthesis and sol-gel processing [6]. Sol-gel processing techniques will be discussed in detail in this chapter because the materials reported in subsequent chapters were fabricated using this method. However, an overview of other techniques usually employed for the synthesis of nanomaterials is also discussed hereunder.
2.2.1. **Combustion route:**

Combustion synthesis leads to highly crystalline particles with large surface areas [7, 8]. The process involves a rapid heating of a solution containing redox groups [9]. During combustion, the temperature reaches approximately 650 °C for one or two minutes making the material crystalline.

2.2.2. **Hydrothermal method:**

Hydrothermal synthesis is typically carried out in a pressurized vessel called an autoclave with the reaction in aqueous solution [10]. The temperature in the autoclave can be raised above the boiling point of water, reaching the pressure of vapour saturation. Hydrothermal synthesis is widely used for the
preparation of metal oxide nanoparticles which can easily be obtained through hydrothermal treatment of peptized precipitates of a metal precursor with water [10, 11]. The hydrothermal method can be useful to control grain size, particle morphology, crystalline phase and surface chemistry through regulation of the solution composition, reaction temperature, pressure, solvent properties, additives and aging time [9].

2.2.3. Gas phase methods:

Gas phase methods are ideal for the production of thin films. Gas phase synthesis can be carried out chemically or physically. Chemical vapour deposition (CVD) is a widely used industrial technique that can coat large areas in a short space of time [9]. During the procedure, metal oxide is formed from a chemical reaction or decomposition of a precursor in the gas phase [12, 13].

Physical vapour deposition (PVD) is another thin film deposition technique. The process is similar to chemical vapour deposition (CVD) except that the raw materials/precursors, i.e. the material that is going to be deposited starts out in solid form, whereas in CVD, the precursors are introduced to the reaction chamber in the gaseous state. The process proceeds atomistically and mostly involves no chemical reactions. Various methods have been developed for the removal of growth species from the source or target. The thickness of the deposits can vary from angstroms to millimeters. In general, these methods can be divided into two
groups: evaporation and sputtering. In evaporation, the growth species are removed from the source by thermal means. In sputtering, atoms or molecules are dislodged from solid target through impact of gaseous ions (plasma) [14].

2.2.4. Microwave synthesis:

Microwave synthesis is relatively new and an interesting technique for the synthesis of oxide materials [15]. Various nanomaterials have been synthesized in remarkably short time under microwave irradiation [16, 17]. Microwave techniques eliminate the use of high temperature calcination for extended periods of time and allow for fast, reproducible synthesis of crystalline metal oxide nanomaterials. Utilizing microwave energy for the thermal treatment generally leads to a very fine particle in the nanocrystalline regime because of the shorter synthesis time and a highly focused local heating.

2.2.5. Sol-gel method:

The sol-gel process is a capable wet chemical process to make ceramic and glass materials. This synthesis technique involves the conversion of a system from a colloidal liquid, named sol, into a semi-solid gel phase [18, 19, 20]. The sol-gel technology can be used to prepare ceramic or glass materials in a wide variety of forms: ultra-fine or spherical shaped powders, thin film coatings, ceramic fibres, microporous inorganic membranes, monolithics, or extremely
porous aerogels. An overview of the sol-gel process is illustrated in Fig. 2.2.

This technique offers many advantages including the low processing temperature, the ability to control the composition on molecular scale and the porosity to obtain high surface area materials, the homogeneity of the final product up to atomic scale. Moreover, it is possible to synthesize complex composition materials, to form higher purity products through the use of high purity reagents. The sol-gel process allows obtaining high quality films up to micron thickness, difficult to obtain using the physical deposition techniques. Moreover, it is possible to synthesize complex composition materials and to provide coatings over complex geometries [18, 19, 20].

**Fig.2.2.** Mechanism of Sol-gel process
The starting materials used in the preparation of the sol are usually inorganic metal salts or metal organic compounds, which by hydrolysis and polycondensation reactions form the sol [18, 19, 20]. Further processing of the sol enables one to make ceramic materials in different forms. Thin films can be produced by spin-coating or dip-coating. When the sol is cast into a mould, a wet gel will form. By drying and heat-treatment, the gel is converted into dense ceramic or glass materials. If the liquid in a wet gel is removed under a supercritical condition, a highly porous and extremely low density aerogel material is obtained. As the viscosity of a sol is adjusted into a suitable viscosity range, ceramic fibres can be drawn from the sol. Ultra-fine and uniform ceramic powders are formed by precipitation, spray pyrolysis, or emulsion techniques.

2.3. Characterization Techniques:

2.3.1. X-ray Diffraction:

The German Physicist, Von Laue in 1912 was the first who took up the problem of X-ray diffraction (XRD) with the cause that, “if crystals were composed of regularly spaced atoms which might act as scattering centers for x-rays, and if X-rays were electromagnetic waves of wavelength about equal to the inter atomic distances in crystals, then it should be possible to diffract X-rays by means of crystals” [21]. Now a days, X-ray diffraction is most extensively used technique for the characterization of the materials. A lot of information can be extracted from the XRD data. This is an
appropriate technique for all forms of samples, i.e. powder and bulk as well as thin film. Using this technique, one can get the information regarding the crystalline nature of a material, nature of the phase present, lattice parameter and grain size [22]. From the position and shape of the lines, one can obtain information regarding the unit cell parameters and microstructural parameters (grain size, microstrain, etc), respectively. In case of thin films, the change in lattice parameter with respect to the bulk gives the idea about the nature of strain present in the system.

The interaction of X-ray radiation with crystalline sample is governed by Bragg’s law, which depicts a relationship between the diffraction angles (Bragg angle), X-ray wavelength, and interplanar spacing of the crystal planes. According to Bragg’s law, the X-ray diffraction can be visualized as X-rays reflecting from a series of crystallographic planes as shown in Fig. 2.3. The path differences introduced between a pair of waves travelled through the neighboring crystallographic planes are determined by the interplanar spacing. If the total path difference is equal to nλ (n being an integer), the constructive interference will occur and a group of diffraction peaks can be observed, which give rise to X-ray patterns. The quantitative account of Bragg’s law can be expressed as:

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

where \( d \) is the interplanar spacing for a given set of \( hkl \) and \( \theta \) the Bragg angle.
Fig. 2.3. Geometrical illustrations of crystal planes and Bragg’s law.

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

Fig. 2.4. X-ray Diffractometer (XRD) machine.

The XRD measurements were carried out using Rigaku X-ray diffractometer with CuKα (\(\lambda = 1.54187\text{Å}\)) radiation at room
temperature, shown in Fig. 2.4, and operated at a voltage of 30kV and filament current of 40mA. The phase identification for all the samples reported in this thesis was performed by matching the peak positions and intensities in XRD patterns to those patterns in the JCPDS (Joint Committee on Powder Diffraction Standards) database.

The diffraction method is based on the effect of broadening of diffraction reflections associated with the size of the particles (crystallites). All types of defects cause displacement of the atoms from the lattice sites. M.A. Krivoglaz in 1969 [23] derived an equation for the intensity of the Bragg reflections from a crystal defect, which enabled all the defects to be derived conventionally into two groups. The defects in the first group only lower the intensity of the diffraction reflections but do not cause the reflection broadening. The broadening of the reflections is caused by the defects of second group. These defects are micro-deformations, inhomogeneity (non-uniform composition of the substance over their volume) and the small particle size. The size of nanomaterials can be derived from the peak broadening and can be calculated by using the Scherrer equation (2.2), provided that the nanocrystalline size is less than 100nm.

\[ D = \frac{k\lambda}{\beta \cos \theta} \]

where D is the average crystallite dimension perpendicular to the reflecting phases, \( \lambda \) the X-ray wavelength, k the Scherrer constant.
which equals 0.9 for spherical particles, whose value depends on the shape of the particle (crystallite, domain) and on diffraction reflection indices (hkl), and $\beta$ is the full width at half maximum of the peaks. The Scherrer formula is quite satisfactory for small grains (large broadening) in the absence of significant microstrain. A microstrain describes the relative mean square deviation of the lattice spacing from its mean value. Based on the grain size dependence of the strain it is reasonable to assume that there is a radial strain gradient, but from X-ray diffraction only a homogeneous, volume-averaged value is obtained.

2.3.2. Scanning Electron Microscopy (SEM):

Electron microscopes are scientific instruments that use a beam of energetic electrons to examine objects on a very fine scale. Electron microscopes were developed due to the limitations of Light Microscopes which are limited by the physics of light. In the early 1930's this theoretical limit had been reached and there was a scientific desire to see the fine details of the interior structures of organic cells (nucleus, mitochondria...etc.). This required 10,000X plus magnification which was not possible using existing optical microscopes.

The first Scanning electron microscope (SEM) debuted in 1938 (Von Ardenne) with the first commercial instruments around 1965. Its late development was due to the electronics involved in "scanning" the beam of electrons across the sample. Scanning electron
microscopy (SEM) can provide a highly magnified image of the surface and the composition information of near surface regions of a material [24]. The resolution of SEM can approach a few nanometers and the magnifications of SEM can be easily adjusted from about 10 times to 300,000 times. In SEM, electron beam, accelerated by a relatively low voltage of 1-20 kV, is scanned on the specimen surface. As the electron beam strikes the surface, a large number of signals are generated from (or through) the surface in the form of electrons or photons. These signals emitted from the specimen are collected by detectors to form images and the images are displayed on a cathode ray tube screen. There are three types of images produced in SEM: secondary electron images, backscattered electron images, and elemental X-ray maps. Secondary electrons (SE) are considered to be the electrons resulted from inelastic scattering with atomic electrons and with the energy less than 50 eV. The secondary emission of electrons from the specimen surface is usually confined to an area near the beam impact zone that permits images to be obtained at high resolution. These images, as seen on a cathode ray tube, provide a three dimensional appearance due to the large depth of field of the SEM as well as the shadow relief of the secondary electrons contrast. Backscattered electrons (BSE) are considered to be the electrons resulted from elastic scattering with the atomic nucleus and with the energy greater than 50 eV [24]. The backscattering will likely occur in a material of higher atomic
number, so the contrast caused by elemental differences can be built up. After the primary electron beam collides with an atom in the specimen and ejects a core electron from the atom, the excited atom then decays to its ground state and emit either a characteristic X-ray photon or an Auger electron [25]. The energy dispersive X-ray detector (EDX) can sort the X-ray signal by energy and produce elemental images, so the spatial distribution of particular elements can be detected by SEM. SEM usually has resolution of 1 nm for 1 KV, even resolution of 0.6 nm is possible for 5 KV.

Fig. 2.5. Schematic details of SEM

2.3.3. **Transmission Electron microscopy (TEM):**

Transmission electron microscopy (TEM) is a microscopy technique where a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through.
An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument’s user to examine fine detail—even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEMs find application in cancer research, virology, materials science as well as pollution 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.

The first TEM was built by Max Knoll and Ernst Ruska in 1931, with this group developing the first TEM with resolving
power greater than that of light in 1933 and the first commercial TEM in 1939.

Theoretically, the maximum resolution, \( d \), that one can obtain with a light microscope has been limited by the wavelength of the photons that are being used to probe the sample, \( \lambda \) and the numerical aperture of the system, \( NA \) [26].

\[
d = \frac{\lambda}{2 n \sin \alpha} \approx \frac{\lambda}{2 NA}
\]

Early twentieth century scientist’s theorized ways of getting around the limitations of the relatively large wavelength of visible light (wavelengths of 400–700 nanometers) by using electrons. Like all matter, electrons have both wave and particle properties (as theorized by Louis-Victor de Broglie), and their wave-like properties mean that a beam of electrons can be made to behave like a beam of electromagnetic radiation. The wavelength of electrons is found by equating the de Broglie equation to the kinetic energy of an electron. An additional correction must be made to account for relativistic effects, as in TEM an electron’s velocity approaches the speed of light, \( c \) [27].

\[
\lambda_e \approx \frac{h}{\sqrt{2m_0E(1 + \frac{E}{2m_0c^2})}}
\]

where, \( h \) is Planck’s constant, \( m_0 \) is the rest mass of an electron and \( E \) is the energy of the accelerated electron. Electrons are usually generated in an electron microscope by a process known as thermionic emission from a filament, usually tungsten, in the same
manner as a light bulb, or alternatively by field electron emission [28]. The electrons are then accelerated by an electric potential (measured in volts) and focused by electrostatic and electromagnetic lenses onto the sample. The transmitted beam contains information about electron density, phase and periodicity; this beam is used to form an image.

![Diagram of TEM components](image)

**Fig.2.6.** Layout of optical components in a basic TEM

**Components:**

A TEM is composed of several components, which include a vacuum system in which the electrons travel an electron emission source for generation of the electron stream, a series of electromagnetic lenses, as well as electrostatic plates. The latter two
allow the operator to guide and manipulate the beam as required. Also required is a device to allow the insertion into, motion within, and removal of specimens from the beam path. Imaging devices are subsequently used to create an image from the electrons that exit the system.

**Fig. 2.7.** Transmission electron microscope (TEM)

*Electron gun:*

The electron gun is formed from several components: the filament, a biasing circuit, a Wehnelt cap, and an extraction anode. By connecting the filament to the negative component power supply, electrons can be "pumped" from the electron gun to the anode plate, and TEM column, thus completing the circuit. The gun is designed to create a beam of electrons exiting from the assembly at some given
angle, known as the gun divergence semi angle, \( \alpha \). By constructing the Wehnelt cylinder such that it has a higher negative charge than the filament itself, electrons that exit the filament in a diverging manner are, under proper operation, forced into a converging pattern the minimum size of which is the gun crossover diameter.

![Cross sectional diagram of an electron gun assembly](image)

**Fig.2.8.** Cross sectional diagram of an electron gun assembly, illustrating electron extraction.

The thermionic emission current density, \( J \), can be related to the work function of the emitting material and is a Boltzmann distribution given below, where \( A \) is a constant, \( \Phi \) is the work function and \( T \) is the temperature of the material [29].

\[
J = AT^2 e^\Phi \exp\left(-\frac{\Phi}{kT}\right)
\]

This equation shows that in order to achieve sufficient current density it is necessary to heat the emitter, taking care not to cause
damage by application of excessive heat, for this reason materials with either a high melting point, such as tungsten, or those with a low work function (LaB$_6$) are required for the gun filament.

Furthermore both lanthanum hexaboride and tungsten thermionic sources must be heated in order to achieve thermionic emission, this can be achieved by the use of a small resistive strip. To prevent thermal shock, there is often a delay enforced in the application of current to the tip, to prevent thermal gradients from damaging the filament, the delay is usually a few seconds for LaB$_6$, and significantly lower for tungsten.

2.3.4. Optical spectroscopy:

Optical spectroscopy has been widely used for the characterization of nanomaterials and the techniques can be generally categorized into two groups: absorption and emission spectroscopy and vibrational spectroscopy. The former determines the electronic structures of atoms, ions, molecules or crystals through exciting electrons from the ground to excited states (absorption) and relaxing from the excited to ground states (emission). The vibrational techniques may be summarized as involving the interactions of photons with species in a sample that results in energy transfer to or from the sample via vibrational excitation or de-excitation. The vibrational frequencies provide the information of chemical bonds in the detecting samples. Infra red
and Raman spectroscopy are the examples of vibrational spectroscopy.

2.3.4.1. UV-Visible Spectroscopy:

_Ultraviolet-visible (UV-vis)_ spectroscopy is widely utilized to quantitatively characterize organic and inorganic nanosized molecules. A sample is irradiated with electromagnetic waves in the ultraviolet and visible ranges and the absorbed light is analyzed through the resulting spectrum [30, 31]. It can be employed to identify the constituents of a substance, determine their concentrations, and to identify functional groups in molecules. The samples can be either organic or inorganic, and may exist in gaseous, liquid or solid form. Different sized materials can be characterized, ranging from transition metal ions and small molecular weight organic molecules, whose diameters can be several Ångstroms, to polymers, supramolecular assemblies, nano-particles and bulk materials. Size dependant properties can also be observed in a UV-visible spectrum, particularly in the nano and atomic scales. These include peak broadening and shifts in the absorption wavelength. Many electronic properties, such as the band gap of a material, can also be determined by this technique. The energies associated with UV-visible ranges are sufficient to excite molecular electrons to higher energy orbitals [32, 33]. Photons in the visible range have wavelengths between 800-400 nm, which corresponds to energies between 36 and 72 kcal/mol. The near UV range includes
wavelengths down to 200 nm, and has energies as high as 143 kcal/mol. UV radiations of lower wavelengths is difficult to handle for safety reasons, and is rarely used in routine UV-vis spectroscopy. Fig. 2.9 shows a typical UV-vis absorption experiment for a liquid sample. A beam of monochromatic light is split into two beams, one of them is passed through the sample, and the other passes a reference (in this figure, a solvent in which the sample is dissolved) [34]. After transmission through the sample and reference, the two beams are directed back to the detectors where they are compared. The difference between the signals is the basis of the measurement.

Liquid samples are usually contained in a cell (called a cuvette) that has flat, fused quartz faces. Quartz is commonly used as it is transparent to both UV and visible lights.

UV-vis spectroscopy offers a relatively straightforward and effective way for quantitatively characterizing both organic and inorganic nanomaterials. Furthermore, as it operates on the principle of absorption of photons that promotes the molecule to an excited state; it is an ideal technique for determining the electronic properties of nanomaterials. In the spectrum of nanoparticles, the absorption peak’s width strongly depends on the chemical composition and the particle size. As a result, their spectrum is different from their bulk counterparts. For instance, for semiconductor nanocrystals, the absorption spectrum is broadened owing to quantum confinement effects, [35, 36] and as their size
reduces, there is no longer a distinct peak, rather there is a band. Furthermore, semiconductor nanoparticle’s absorption peaks shift towards smaller wavelengths (higher energies) as their crystal size decreases [36-39]. An important consequence of using the UV-vis spectroscopy is that the band gap of nanosized materials can be determined.

![Schematic of UV-Visible spectrophotometer](image)

**Fig. 2.9.** A schematic representation of UV-Visible spectrophotometer

**2.3.4.2. Photoluminescence (PL) Spectroscopy:**

*PL spectroscopy* concerns monitoring the light emitted from atoms or molecules after they have absorbed photons [40, 41]. It is suitable for materials that exhibit photoluminescence. PL spectroscopy is suitable for the characterization of both organic and inorganic materials of virtually any size, and the samples can be in solid, liquid, or gaseous forms. Electromagnetic radiation in the UV and visible ranges is utilized in PL spectroscopy. The sample’s PL emission properties are characterized by four parameters: intensity, emission wavelength, bandwidth of the emission peak, and the
emission stability [42]. The PL properties of a material can change in different ambient environments, or in the presence of other molecules. Furthermore, as dimensions are reduced to the nanoscale, PL emission properties can change, in particular a size dependent shift in the emission wavelength can be observed. Additionally, because the released photon corresponds to the energy difference between the states, PL spectroscopy can be utilized to study material properties such as band gap, recombination mechanisms, and impurity levels. In a typical PL spectroscopy setup for liquid samples (Fig. 2.10), a solution containing the sample is placed in a quartz cuvette with a known path length. Double beam optics is generally employed. The first beam passes through an excitation filter or monochromator, then through the sample and onto a detector. This impinging light causes photoluminescence, which is emitted in all directions. A small portion of the emitted light arrives at the detector after passing through an optional emission filter or monochromator [43]. A second reference beam is attenuated and compared with the beam from the sample. Solid samples can also be analyzed, with the incident beam impinging on the material (thin film, powder etc.). Generally an emission spectrum is recorded, where the sample is irradiated with a single wavelength and the intensity of the luminescence emission is recorded as a function of wavelength. The fluorescence of a sample can also be monitored as a
function of time, after excitation by a flash of light. This technique is called *time resolved fluorescence spectroscopy*.

**Fig. 2.10.** PL spectrophotometer set up

### 2.3.4.3. Infrared Spectroscopy:

*Infrared (IR) spectroscopy* is a popular characterization technique in which a sample is placed in the path of an IR radiation source and its absorption of different IR frequencies is measured [44, 45]. Solid, liquid, and gaseous samples can all be characterized by this technique. IR photons energies, in a range between 1 to 15 kcal/mol, are insufficient to excite electrons to higher electronic energy states, but transitions in vibrational energy states (see Fig.
2.11). These states are associated with a molecule’s bonds, and consequently

![Energy Level Diagram](image)

**Fig. 2.11.** Possible physical processes following absorption of a photon

Each molecule has its own unique signatures. Therefore, IR spectroscopy may be employed to identify the type of bond between two or more atoms and consequently identify functional groups. IR spectroscopy is also widely used to characterize the attachment of organic ligands to organic/inorganic nanoparticles and surfaces. Because IR spectroscopy is quantitative, the number of a type of bond may be determined. Virtually all organic compounds absorb IR radiation, but inorganic materials are less commonly characterized, as heavy atoms show vibrational transitions in the far IR region, with
some having extremely broad peaks that hampers the identification of the functional groups. Furthermore, the peak intensities of some ionic inorganic compounds may be too weak to be measured \[46, 47\]. The covalent bonds that hold molecules together are neither stiff nor rigid, but rather they vibrate at specific frequencies corresponding to their vibrational energy levels. The vibration frequencies depend on several factors including bond strength and the atomic mass. The bonds can be modified in different ways, in a similar manner to a spring. Chemical bonds may be contorted in six different ways: stretching (both symmetrical and asymmetrical), scissoring, rocking, wagging, and twisting. Absorption of IR radiation causes the bond to move from the lowest vibrational state to the next highest, and the energy associated with absorbed IR radiation is converted into these types of motions \[48, 49, 50\] Other rotational motions usually accompany these individual vibrational motions. These combinations lead to absorption bands, not discrete lines, which are commonly observed in the mid IR region \[50\]. Weaker bonds require less energy to be absorbed and behave as though the bonds are springs that have different strengths. More complex molecules contain dozens or even hundreds of different possible bond stretches and bending motions, which implies the spectrum may contain dozens or hundreds of absorption lines. This means that the IR absorption spectrum can be its unique \textit{fingerprint} for identification of a molecule \[51\]. The \textit{fingerprint region} contains wavenumbers between 400 and
1500 cm\(^{-1}\). A diatomic molecule, that has only one bond, can only vibrate in one direction. For a linear molecule (e.g. hydrocarbons) with \(n\) atoms, there are \(3n-5\) vibrational modes. If the molecule is non-linear (such as methane, aromatics etc.), then there will be \(3n-6\) modes. Samples can be prepared in several ways for an IR measurement. For powders, a small amount of the sample is added to potassium bromide (KBr), after which this mixture is ground into a fine powder and subsequently compressed into a small, thin, quasi-transparent disc (Fig. 2.11). For liquids, a drop of sample may be sandwiched between two salt plates, such as NaCl, KBr and NaCl are chosen as neither of these compound shows an IR active stretch in the region typically observed for organic and some inorganic molecules.

![Fig.2.12. Various processes to take the IR spectra](image)

**2.3.5. Electron spectroscopy:**

In this section we shall discuss Energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The electron spectroscopy relies on the unique energy levels of the emission of photons (X-ray) or electrons ejected from the atoms in
question. When an incident electron or photon, such as X-ray or γ-ray, strikes an unexcited atom, an electron from an inner shell is ejected and leaves a hole or electron vacancy in the inner shell. An electron from an outer shell fills the hole by lowering its energy, and simultaneously the excess energy is released through either emission of an X-ray, which is used in EDS, or ejection of a third electron that is known as auger electron, from a further outer shell, which is used in Auger Electron spectroscopy (AES). If incident photons are used for excitation, the resulting characteristic X-rays are known as fluorescent X-rays. Since each atom in the Periodic Table has a unique electronic structure with unique set of energy levels, both X-ray and Auger spectral lines are characteristic of the element under investigation. By measuring the energies of the X-rays and Auger electrons emitted by a material, its chemical composition can be determined.
A similar principle is applicable to XPS. In XPS, relatively low energy X-rays are used to eject the electrons from an atom via the photoelectric effect. In XPS the sample is irradiated with a beam of usually monochromatic, low-energy X-rays. Photoelectron emission results from the atoms in the specimen surface, and the kinetic energy distribution of the ejected photoelectrons is measured directly using an electron spectrometer. Each surface atom possesses core-level electrons that are not directly involved with chemical bonding but are influenced slightly by the chemical environment of the atom.
The binding energy of each core-level electron (approximately its ionization energy) is characteristic of the atom and specific orbital to which it belongs. Since the energy of the incident X-rays is known, the measured kinetic energy of a core-level photoelectron peak can be related directly to its characteristic binding energy. The binding energies of the various photoelectron peaks (1s, 2s, 2p, etc.) are well tabulated and XPS therefore provides a means of elemental identification which can also be quantified via measurement of integrated photoelectron peak intensities and the use of a standard set of sensitivity factors to give a surface atomic composition. The low binding energy region of the XPS spectrum is usually excited with a separate ultraviolet photon source, such as a helium lamp, (ultraviolet photoelectron spectroscopy, UPS) and provides data on the valence band electronic structure of the surface [52].

**Fig.2.14.** Photoelectron emission in XPS
References:


69


