

CHAPTER II

EXPERIMENTAL PROCEDURES AND CHARACTERIZATION TECHNIQUES

2.1 Combustion basics

Combustion is a conversion of the substance called a fuel into chemical compounds known as products of combustion in combination with an oxidizer. The combustion process is an exothermic chemical reaction, i.e., a reaction that releases energy as it occurs. This combustion may be represented symbolically by:



Here the fuel and the oxidizer are reactants. This relation indicates that the reactants produce combustion products and energy. Either the chemical energy released is transferred to the surroundings as it is produced, or it remains in the combustion products in the form of elevated internal energy (temperature), or some combination.

2.2. Principles of combustion

The basis of the combustion synthesis technique comes from the thermochemical concepts used in the field of propellants and explosives. The reaction releases maximum energy when the reductive mixture follows its chemical formula. That is, the element valences are balanced, irrespective of whether they are present in the oxidizer or the fuel components of the mixture. Thus, the method consists of establishing a simple valence balance and the assumed valences are those presented by the elements in the usual products of the combustion reaction, which are CO₂, H₂O and N₂. The extrapolation of this concept to combustion synthesis of ceramic oxides means that metals should also be considered as reducing elements with the valences they have in the corresponding oxides. Experimentally, the chemical balance is used to calculate the appropriate amounts of the selected starting materials (i.e. the cationic precursors and the fuel) following its chemical formula designed for expected product composition. This concept is particularly useful when thermodynamic calculations are difficult to carry out for lack of the relevant parameters and it has been shown that there is a direct correlation between the results derived from the valence balance and

those based on the heat of formation or bond energies. When both the precursor salts and the fuel are water soluble, a good homogenization can be achieved in the solution. There are a number of reaction parameters which affect combustion synthesis reactions, e.g. reactant particle size, stoichiometry (including the use of diluents or inert reactants), green density, thermal conductivity, ignition temperature, heat loss and, therefore, combustion temperature, heating and cooling rates and physical conditions of reactants (solid, liquid, gas). Many of these parameters are interdependent and have a significant effect on the final product morphology and properties. Establishing the optimum reaction parameters for synthesizing a material is based on obtaining a fundamental understanding of the controlling reaction mechanisms in each combustion reaction system. This has been one of the most active research areas for combustion synthesis. Combustion synthesis has emerged as an important technique for the synthesis and processing of advanced ceramics, catalysts and composite alloys inter-metallic and nanometer-sized materials.

2.3 Three temperature of combustion

The objective of good combustion is to release all the heat in the fuel. This is accomplished by controlling the “three T’s” of combustion which are 1) temperature high enough to ignite and maintain ignition of the fuel, 2) turbulence or intimate mixing of the fuel and oxygen and 3) time, sufficient for complete combustion. Commonly used fuels like natural gas and propane generally consist of carbon and hydrogen. Water vapour is a by-product of burning hydrogen. This removes heat from the fuel gases, which would otherwise be available for more heat transfer. Natural gas contains more hydrogen and less carbon per kg than fuel oils and produces more water vapour. Consequently, more heat will be carried away from exhaust while firing natural gas. Too much or too little fuel with the available combustion air may potentially result in unburned fuel and carbon monoxide generation. A very specific amount of O₂ is needed for perfect combustion and some additional (excess) air is required for ensuring complete combustion. However, excess air will result in heat and efficiency losses. Not all of the fuel is converted to heat and absorbed by the steam generation equipment. Usually all the hydrogen in the fuel is burned and more boiler fuels are allowable with today’s air pollution standards, contain little or no sulfur. So the main challenge in combustion efficiency is directed toward unburned carbon (in the ash or incompletely burned gas), which forms CO instead of CO₂.

2.4 Overview of combustion synthesis

Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an effective, low-cost method for production of various industrially useful materials. Today CS has become a very popular approach for preparation of nanomaterials and is practiced in 65 countries. Recently, a number of important breakthroughs in this field have been made, notably for the development of new catalysts and nano carriers with properties better than those of similar traditional materials. The extensive research carried out in the last five years emphasized the SHS capabilities for material improvement, energy saving and environmental protection. The importance of industrialization of the SHS process is also realized through several books [1,2] and reviews [3-6]. Combustion synthesis (CS) has attracted considerable interest in the last two decades due to its unique combination of technologically relevant characteristics. The method, in fact, makes possible the rapid synthesis of several highly refractory inorganic materials and advanced ceramics, thus avoiding the prolonged high temperature treatment, known as sintering, usually required in their conventional preparation. Refractory materials are resistant to thermal shock and are used to make crucibles, incinerators, insulation and furnaces, particularly metallurgical furnaces. Advanced ceramics are inorganic, nonmetallic, crystalline materials of severely controlled composition and manufactured with detailed regulation from highly refined raw materials giving the products precisely specified attributes desired by the producer. Reaction sintering is the welding together of small particles of a ceramic material applying prolonged heat below the melting point resulting in improved mechanical and physical properties of the material. In this novel approach, the synthesis is obtained through an extremely rapid self-sustaining process driven by a large heat release with the internal energy of the reactants. The macroscopic characteristics of CS procedure resemble those observed in conventional combustion processes. The reactants, in the form of fine powders and these mixtures are then placed in a controlled atmosphere and ignited through a resistively heated wire, a laser beam, or an electric discharge. Due to the enthalpy change between the reactants and products SHS reactions generally result in high combustion temperatures. The combustion synthesis reaction can be conducted in two modes [7].

Combustion synthesis methods can be separated into three categories there are:

- Conventional self-propagating mode (SHS) of nanoscale materials, i.e. initial reactants are in solid state (condensed phase combustion).
- Volume combustion synthesis (VCS) i.e. initial reactants are in solid state (reactants are heated by an external source)
- Solution-combustion synthesis (SCS) of nanosized powders, i.e. initial reaction medium is aqueous solution.

2.4.1 Conventional SHS: condensed phase combustion

It is not an easy task to produce nanomaterials by conventional SHS, where the typical scale of heterogeneity for the initial solid reactants is on the order of 10-100 nm. This feature, coupled with high reaction temperatures (>2000 K), makes it difficult to synthesize nanosize structures with high surface area. However, several methods were suggested for synthesis of nanomaterials by using this approach: (i) SHS synthesis, followed by intensive milling; (ii) SHS + mechanical activation (MA); (iii) SHS synthesis followed by chemical treatment, so-called chemical dispersion; (iv) SHS with additives; (v) carbon combustion synthesis (CCS). Since the first method is common and well known [8] and different combinations of SHS and MA have already been well documented [9], the abilities of three other methods are briefly discussed below. The process of etching SHS powders in an appropriate dilute acid (e.g. HNO₃ or H₂SO₄) solution, thus dissolving the defect-rich layers between the crystallites and removing impurities, followed by ball milling, is termed as chemical dispersion. This approach was suggested by the group from the Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences [10]. A variety of fine powders including boron, aluminium and silicon nitrides were produced by this technique. The SHS method with additives for nanomaterial synthesis is known as alkali metal molten salt assisted combustion [11]. In this process, the reducing metal, (e.g. Sn) reacts with transition metal oxide (SnO_x) in the melt of the alkali metal salt (e.g. NaCl) to form fine reduced metal particles (Sn).

2.4.2 Volume combustion synthesis (VCS)

The reactants are heated by an external source (e.g., tungsten or molybdenum coil, laser) either locally in SHS or uniformly in a furnace or microwave in the VCS to initiate an exothermic reaction. It is interesting to note that many combustion synthesis reactions lie between these two types described. If the combination of thermo chemical and thermo physical properties of the system are appropriate, a high temperature reaction front (usually 1500-4000°C) is initiated which then propagates through the mixture with a rate ranging from some millimetres to several centimetres per second for micron sized powders. The initial mixture heats up and the contact between particles of starting mixtures is too limited for a chemical reaction to occur. Once the mixture's temperature rises to a certain point, impurities escape. Next, the reactant with the lowest melting point coats other particles increasing the contact among the powders. At this stage, the chemical reaction is ignited. At the combustion zone, the leading edge of the heat wave promotes a full-blown reaction. Here, initial products are formed which may or may not be the same composition as the final products. Next, the final products begin to form from the heat released from the combustion wave followed by crystal growth and organization. Finally, the mixture cools into the final product [12]. A variant of this scheme involves one gaseous reactant. In this case, the reaction mixture is made of the powder(s) of the other non-gaseous reactant(s). This approach allows the synthesis of nitrides, hydrides and oxides. Beside low energy requirements and higher reaction rate, the method has other advantages over the traditional methods, such as the simplicity of the experimental apparatus. Another demonstrated advantage is represented by the high purity of the products, which is largely due to the expulsion of volatile impurities under the extremely high temperatures in the wave. The reaction products are generally porous, but densification can easily be obtained through the application of a mechanical load just after the end of the reaction or simultaneous to it. Also, the high thermal gradients and the rapid cooling rate can give rise to new non-equilibrium or metastable phases.

2.4.3 Solution combustion synthesis (SCS)

Solution Combustion Synthesis (SCS) is a versatile, simple, rapid and single step process, which involves a self-sustained reaction in homogeneous solution of different oxidizers (e.g., metal nitrates) and fuels (e.g., urea, glycine, citric acid and

hydrazides). Depending on the type of the precursors, as well as on the conditions used for the process organization, the SCS may occur as either volume or layer-by-layer propagating combustion modes [13]. The most important fact about SCS is that it is a short duration process and the various gases formed during the process inhibit particle size growth, which favours the formation of nano-sized powders [14]. The choice of fuel for the SCS is the most important factor. The glycine and citric acid have been adopted for the synthesis of metal/metal oxide nanoparticles because they are widely used for the synthesis of nanomaterials. Among known fuels, glycine has demonstrated the versatility of combustion methods by the successful preparation of a large number of single phase, well crystallized, multi component oxides. Also it is inexpensive and its combustion heat (-3.24 kcal/g) is more negative compared with urea (-2.98 kcal/g). When citric acid is employed in a combustion process, the heat released in combustion is more and as a result the combustion enthalpy is more which is responsible for the growth of the sample and complete combustion reaction with more crystalline phase takes place. The citric acid and glycine are considered to be ideal fuels because (i) they act as a good source of N, C and H, which on combustion evolve N_2 , CO_2 and H_2O gases, favoring the formation of nanoparticles, (ii) they form complexes with the metal ions facilitating homogenous mixing of the cations in solution and (iii) these fuels are water soluble and good homogenization can be achieved in solution. A number of preparation methods and techniques have been examined for identifying the most reliable and cheapest method of producing nanomaterials. However, these methods require specific apparatus, vacuum conditions and high cost equipment, but the solution combustion method is an alternative quick process, low cost method and prepared a large amount of nanopowders. A few publications described the fabrication of metal oxide semiconductor nanopowders by solution combustion method. However, it is a challenge to find an efficient and simple way, using low temperature and convenient method suitable for large scale production of metal oxide semiconductor powders with particle size about several nanometres by using this method.

2.5 Preparative Methods

2.5.1. Preparation of nanoparticles by solution combustion method (SCS)

For the preparation of nanoparticles, the corresponding metal nitrate (oxidizer) was taken as a precursor and glycine or citric acid was used as fuel. The stoichiometric composition of the solution components (fuels and oxidizer) was calculated according to the principle of propellant chemistry, keeping the oxidizer (metal nitrate) to fuel (glycine or citric acid) ratio as unity. In the combustion reaction, the molar ratio (ψ) is defined as the ratio of fuel to metal nitrate and it corresponds to the situation of an 'equivalent stoichiometric ratio' which implies that the oxygen content of metal nitrate can be completely oxidized or it can consume fuel exactly. As a result, metal or metal oxide product and gases of CO₂, H₂O and N₂ can be formed directly from the reaction between the fuel and the oxidizer without the need of getting oxygen from outside. The solution was kept in the hotplate at 300°C. With the large amount of fumes produced the combustion reaction was completed and loose powder was formed, which was crushed and ground thoroughly.

2.5.2 Calculation of the elemental stoichiometry coefficient (ESC) and determining the stoichiometry of fuel – oxidizer mixture

The oxidizer/fuel molar ratio required for a stoichiometric mixture (ESC, $\Phi_e = 1$) is determined by summing the total oxidizing and reducing valencies in the oxidizer compounds and dividing by the sum of the total oxidizing and reducing valencies in the fuel compounds. Oxygen is considered to be the only oxidizing element (+2), carbon (-4), hydrogen (-1) and metal cations are reducing elements.

$$\Phi_e = \frac{\sum (\text{Coefficient of oxidizing elements in specific formula}) \times (\text{oxidizing valency})}{(-1) \sum (\text{Coefficient of reducing elements in specific formula}) \times (\text{reducing valency})}$$

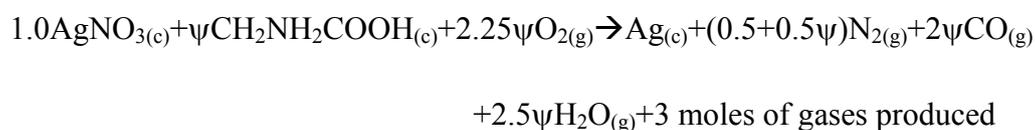
Example: For Ag nanoparticles formation; AgNO₃ (oxidizer), glycine (fuel, NH₅C₂O₂)

$$\begin{aligned}\Phi_e &= \frac{[(1Ag \times -1) + (1N \times 0) + (3O \times 2)]}{(-1)[(2C \times -4) + (1N \times 0) + (5H \times -1) + (2O \times 2)]} \\ &= 5/9 = 0.55\end{aligned}$$

Thus, metal nitrate: glycine molar ratio= 0.55. This ratio is needed for $\Phi_e = 1$, which implies complete combustion of all components. The fuel-stoichiometric composition indicates $\Phi_e = 1$, while fuel lean composition range shows $\Phi_e > 1$ and fuel rich composition range means $\Phi_e < 1$, respectively.

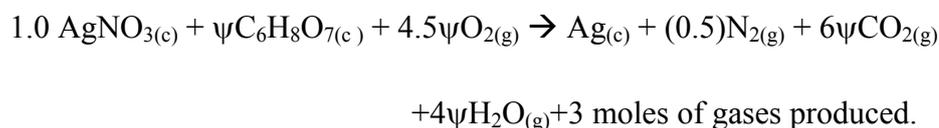
2.5.3 Preparation of silver nanoparticles

For the preparation of silver nanoparticles (Ag NPs), silver nitrate (AgNO_3), glycine ($\text{CH}_2\text{NH}_2\text{COOH}$) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) were taken as starting materials (AR grade). The stoichiometries amount of AgNO_3 and glycine were mixed in 1:0.5 ratios and added to 25 ml distilled water in a crucible. The ratio of the fuel to oxidizers was taken as one ($\phi_e = 1$). The entire mixture was mixed on a magnetic stirrer up to 30 min. It formed a completely aqueous solution, after that the mixture of solution is placed on hot plate at 300°C . The solution boils and dehydrate on reaching the combustion point large amount of fumes are discharged and finally the greyish residue is left behind (which is the silver) which is ground into powder using a mortar pistol. The expected combustion reaction to form Ag NP is:



Here $\psi = 0.555$ and corresponds to the situation of an 'equivalent stoichiometric ratio' which implies that the oxygen content of silver nitrate can be completely oxidized or it can consume glycine exactly.

Citric acid is oxidized by nitrate and serves as fuel. The expected combustion reaction to form Ag NPs is:



where ψ is defined as the molar ratio of citric acid to silver nitrate. Here $\psi = 0.277$ and corresponds to the situation of an 'equivalent stoichiometric ratio' which implies that the oxygen content of silver nitrate can be completely oxidized or it can consume citric acid exactly.

2.6 Characterization techniques

Synthesized Ag nanoparticles were characterized for their structural, surface morphological and optical properties. Field Emission Scanning Electron Microscopy (FESEM) with EDX was used to detect the composition and topography information of the samples. High Resolution Transmission Electron Microscopy (HRTEM) was used to identify the morphology. X-ray Diffraction (XRD) was used to identify the polymorphism, component composition, crystal size and crystal lattice structure. Spectroscopic characterization is utilized to determine the intermolecular interaction and chemical reactions through the intra molecular interactions. The optical absorbance was obtained by UV-Visible spectrophotometer (UV-vis) and Raman Spectroscopy.

2.6.1 UV-Visible Spectrophotometer

UV-visible spectroscopy is widely used in the study of nanomaterials as a diagnostic of nanoparticles formation. Used in conjunction with affinity labelling, UV-visible spectroscopy often provides the means of choice to gauge response in an analysis using nanoparticles. It has been further suggested that the spectroscopic properties of nanoparticles can provided an indicator of their size distribution by fitting the position of the surface plasmon resonance (SPR) to a simple wavelength function. Ultraviolet spectroscopy is a technique used to quantify the light that is adsorbed and scattered by a sample (a quantify known as the extinctions, which is defined as the sum of adsorbed and scattered light [15]. Nanoparticles have optical properties that are sensitive to size, size concentration state, and refractive index near the nanoparticles surface, which makes UV/Vis/IR spectroscopy a valuable tool for identifying, characterizing and studying these materials. Nanoparticles made from certain metals, such as gold and silver strongly interact with specific wavelength of light and the unique optical properties of these materials is the foundation for the field of Plasmonics.

UV spectrometers consist of a light source, reference and sample beams, a monochromator and a detector. The ultraviolet spectrum for a compound is obtained by exposing a sample of the compound to ultraviolet light from a light source, such as Xenon lamp. The energy involved in the electronic transition is large. The absorption takes place in UV with small energies. The wavelength range of UV radiation starts at

the blue and ends at the visible light region at 2000Å. The UV region is sub-divided into two spectral regions namely, near UV region (region between 2000Å - 4000Å) and farer vacuum UV region (region below 2000Å).

The reference beam travels from the light source to the detector without interacting with the sample in the spectrophotometer. The sample beam interacts with the sample exposing it to ultraviolet light of continuously changing wavelength. Energy is absorbed, when the emitted wavelength corresponds to the energy level which promotes an electron to a higher molecular orbital. The ratio between the reference and sample beam intensities (I_0/I) is recorded by the detector. The computer determines at what wavelength the sample absorbs a large amount of ultraviolet by scanning for the largest gap between the two beams. When the sample beam intensity is significantly weaker than the reference beam, there is a large gap between intensities. The computer plots this wavelength as having the highest ultraviolet light absorbance when it prepares the ultraviolet absorbance spectrum. The Beer-Lambert law is most often used in a quantitative way to determine the concentrations of an absorbing species in solution.

$$A = \log (I_0/I) = a*b*c$$

where, A is a measured absorbance in absorbance units (AU), I_0 is a intensity of the incident light at a given wavelength, I is a transmitted intensity, a is a constant known as molar absorptive, b is a path length through the sample, c is a the concentration of the absorbing species

2.6.1.1 Instrumentation

The instrumentation associated with UV spectrophotometer method is outlined schematically in Figure 2.2. The components of this generalized instrument are as described below.

(a) Radiation sources

Radiation sources in absorbance spectrophotometer have two basic requirements. Firstly they must provide sufficient radiant energy over the wavelength region where absorption is to be measured. Second, they should maintain a constant intensity over the time interval during which measurements are made. The radiation

sources of an ultraviolet spectrometer can be either of hydrogen or deuterium discharge lamps or incandescent filament lamps.

(b) Wavelength selection

Spectrophotometric methods usually require the isolation of discrete bands of radiation. The wavelength selection includes filters and monochromators. Filters provide high radiation throughput, approximately 50%-80% efficiency. Such filters may be an absorption filter or an interference filter. A monochromator consists, in general, of (1) an entrance slit that provides a narrow optical image of the radiation source, (2) a collimator that renders the radiation emanating from the entrance slit parallel, (3) a grating or prism for dispersing the incident radiation, (4) a collimator to reform images of the entrance slit or the exit slit, and (5) an exit slit to isolate the desired spectral band by blocking all of the dispersed radiation except that within the desired range.

(c) Detectors

A detector is a transducer that converts electromagnetic radiation into an electron flow, subsequently, into a current flow or voltage in the readout circuit. The important characteristics of any type of detector are spectral sensitivity, wavelength response, gain, and response time.

(d) Readout modules

After the amplification of signals by an ac amplifier, the signal is converted back into dc by a demodulator or rectifier because all the commonly used readout devices require dc signals. A current is usually converted to a voltage before display or recording.

2.6.1.2 Applications

UV-Vis Spectrophotometer is used for the following applications.

- ❖ Identification of various hydrocarbons, vitamins, steroids and conjugate aliphatics.
- ❖ Identification of degradation products.
- ❖ Detection of functional groups.
- ❖ Determination of organic substance etc.,

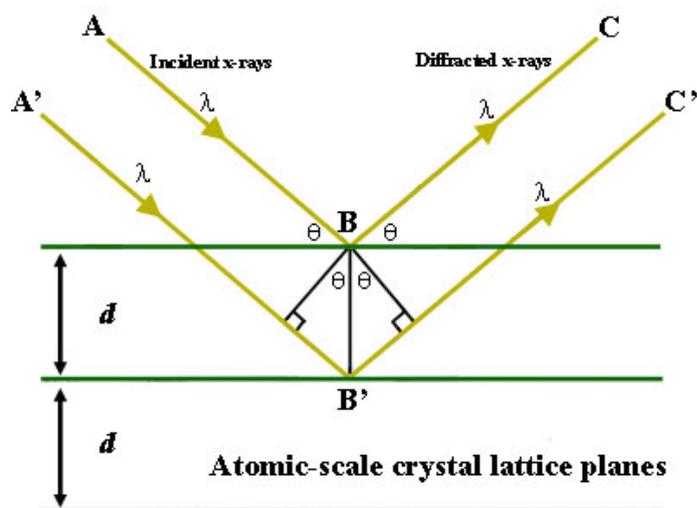
2.6.2 X-ray diffractometer (XRD)

X-Ray diffraction is one of the most important non-destructive tools to analyze all kinds of matter-ranging from fluids, to powders and crystals. XRD is an indispensable method for structural materials characterization and quality control which makes use of the Debye-Scherrer method. This technique uses X-ray or neutron diffraction on powder or microcrystalline samples, where ideally every possible crystalline orientation is represented equally.

X-Ray crystallography method determines the arrangement of atoms within a crystal. A beam of x-ray strikes a crystal and diffracts it into many specific directions. As the crystals are regular arrays of atoms, the x-ray waves are scattered primarily through the atom electrons. Secondary spherical waves are produced when the x-ray strikes the electron. Regular arrays of spherical waves are produced by a regular array of electrons. These waves cancel one another out in most directions through destructive interference, and add constructively in a few specific directions, determined by Bragg's law:

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

where, d is a lattice spacing, θ is a angle of incidence, λ is a wavelength of the incident x-ray beam, n is a integer. Diffraction of X-rays by crystal planes followed as:



2.6.2.1 Instrumentation

The instrumentation associated with X-ray method is outlined schematically in Figure 2.5. The components of this generalized instrument are as described below.

(a) X-ray generating equipment

The modern X-ray tube is a high-vacuum, sealed-off unit. The target is viewed from a very small angle above the surface. The X-ray beam passes out of the tube through a thin window of beryllium or a special glass. Commonly X-ray tubes are operated at 50 or 60 kV. The sensitivity of analysis is also greater because a higher voltage increases the intensity of lines emitted by the X-ray tube target.

(b) Collimators

Radiation from an X-ray tube is collimated either by a series of closely spaced parallel metal plates or by a bundle of tubes, 0.5 mm or smaller in diameter. In a fluorescence spectrometer, one collimator is placed between specimen and analyzer and the other is placed between the analyzer crystal and detector. Increased resolution is obtained by decreasing the separation between the metal plates of the collimator or by increasing the length of the unit.

When the wavelengths of two spectral lines are nearly the same and there is an element with an absorption edge at a wavelength between the lines, that element may be used as a filter to reduce the intensity of the line with the shorter wavelengths.

(c) Analyzing crystals

Virtually monochromatic X radiation is obtained by reflecting X-rays from crystal planes. The relationship between the wavelength of the X-ray beam, the angle of diffraction θ , and the distance between each set of atomic planes of the crystal lattice d , is given by the Bragg condition.

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

(d) Detectors

The detectors used for the detection of radiations may be either of the following, photographic emulsions, the ionization chamber, the Geiger counter, proportional counter, scintillation counter and semiconductor detectors.

2.6.2.2 Applications

The uses of XRD as a non-destructive technique are

- ❖ To identify atomic arrangement.
- ❖ To determine structural properties such as lattice parameters, grain size, phase composition, thermal expansion, epitaxy etc.
- ❖ To identify crystalline phases and orientation.
- ❖ To measure d spacing.
- ❖ To obtain integrated intensities.
- ❖ To compare data with known standards in the JCPDS file, which are for random orientations.

2.6.3 Field Emission Scanning Electron Microscopy (FESEM)

The Scanning Electron Microscope (SEM) is one of the most widely used instruments in materials research laboratories and is common in various forms in fabrication plants. The SEM provides information relating to topographical features, morphology, phase distribution, compositional differences, crystal structure, crystal orientation and the presence and location of electrical defects. The strength of the SEM lies in its inherent versatility due to the multiple signals generated, simple image formation process, wide magnification range, and excellent depth of field [16].

Scanning Electron Microscopy, as the name suggests, scans the sample. Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence- CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples. X-rays generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength. Thus, characteristic X-rays are produced for each element in a mineral that is “excited” by the electron beam. SEM analysis is considered to be “non-destructive”; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

$$\text{Magnification} = \frac{\text{area scanned on the monitor}}{\text{area scanned on the specimen}}$$

Accelerated electrons in a SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons, back scattered electrons, and diffracted backscattered electrons that are used to determine crystal structures and orientations of photons, visible light and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples. X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength. Thus, characteristic X-rays are produced for each element in a mineral that is “excited” by the electron beam. SEM analysis is considered to be “non-destructive”; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

2.6.3.1 Instrumentation

The instrumentation associated with Scanning Electron Microscopy is outlined schematically in Figure 2.4. The components of this sweeping instrument are as described below.

(a) Electron gun

The electron gun produces an electron beam. Its construction is shown in fig. note that this is a thermionic emission gun (TE gun). Thermoelectrons are emitted from a filament (cathode) made of a thin tungsten wire (about 0.1mm) by heating the filament at high temperature (about 2800K). These Thermoelectrons are gathered as an electron beam, flowing in to the metal plate (anode) by applying a positive voltage (1 to 30kV) to the anode. If a hole is made at the center of the anode, the electron beam flows through this hole. When we place an electrode (called a wehnelt electrode) between the cathode and anode and apply a negative voltage to it, we can adjust the current of the electron beam. At this time, the electron beam is finely focused by the action of the wehnelt electrode. The finest point of the beam called the cross over and diameter of 15 to 20 μ m.

The TE gun, explained here, is most generally used. A LaB₆ single crystal is also used as a cathode, but it requires a higher vacuum because of its high activity. Other electron guns are the field-emission gun (FE gun). An electron gun that is used for a high-resolution SEM is the FE gun. The FE gun utilizes the field-Emission effect that take place when a high electric field is applied to a metal surface. The cathode is made of a thin tungsten wire. A tungsten single crystal is welded to this tungsten wire and the tip of the tungsten single crystal is shaped to be a curvature radius of about 100nm. This called the emitter when a positive voltage (a few kV) is applied to a metal plate (extracting electrode) the tunneling effect occurs and electrons are emitted from the emitter. If a hole is made at the center of the extracting electrode, the emitted electron beam flows through this hole then, when we apply a voltage to the electrode (accelerating electrode) located below the extracting electrode, we can be obtain an electron beam having certain energy. In order to generate a field emission, the tip of the emitter must be very clean. Thus, the FE gun needs to be placed in an ultra high vacuum of about 10⁻⁸ Pa.

The electron beam emitted from the emitter behaves as if the beam was emitted from a small electron with diameter of 5 to 10nm. In the case of the TE gun its electron source is 10 to 20μm in diameter, indicating that the FE gun produces a much smaller electron source than the TE gun, thus suitable for high-resolution SEMs. In addition, another advantage of the FE gun is that the energy spread of the electron beam is small because the FE guns require no heating of the emitter. In low-accelerating voltage observation, this energy spread determines the resolution (chromatic aberration); therefore it is very important.

(b) Condenser lens and objective lens

Placing a lens below the electron gun enables us to adjust the diameter of the electron beam. A fine electron beam (probe) is required for the SEM. Two stage lenses, which combine the condenser and objective lenses, are located below the electron gun is focused by the two-stage lenses and a small electron probe is produced.

Role of condenser lens

If the lens action of the condenser lens is strengthened the electron probe become narrower with a smaller ratio b/a , where as if weakened, the electron probe between the condenser lens and objective lens. The 'aperture' made of a thin metal plate, has a small hole. The electron beam, which passed through the condenser lens, illuminates this 'aperture'-plate. The aperture allows a part of electron beam to reach the objective lens. If excitation of the condenser lens is increased, the electron beam greatly broaden on the aperture and therefore, the number of the electrons (amount of probe current) racing the objective lens is decreased, the electron beam does not broaden very much and most of the electron pass through the aperture and many electron reach the objective lens. That is, the adjustment of the excitation of the condenser lens enables we to changes the electron-probe diameter and probe current. However, even if the excitation of the condenser lens is infinitely increased, the diameter of the electron probe does not become infinitely.

Role of the objective lens

To objective lens is used focusing and this lens is a very important lens that determine the final diameter of the electron probe. If the performance of the objective lens is not good, an optimally-fine electron probe cannot be produced despite all of the efforts before the action of the objective lens thus, it is crucial; of the objective lens with the best performance.

(c) Secondary electron detector

The secondary electron detector is used for detecting the secondary electrons emitted from the specimen. A scintillated (fluorescent substance) is coated on the tip of the detector and a high voltage of about 10kV is applied to it. The secondary electrons from the specimen are attracted to this high voltage and then generate light when they hit the scintillated. This light is directed to a photo-multiplier tube (PMT) through a light guide. Then, the heights are converted to electrons, and these electrons are amplified as an electrical signal. A supplementary electrode, called the collector, is placed before the scintillated. In general, in order to help the scintillated acquire secondary electrons, a few hundred volts is applied to this collector. By changing this voltage we can control the number of secondary electrons to be collected. This type of the detector was originally developed by everhart and thornly, so this SEMs incorporate this detector in the specimen chamber, however, when a SEM is equipped with a strongly excited objective lens for higher resolution, a secondary electron

detector is placed above the objective lens and secondary electron are detected by utilizing the lens magnetic fields. This detector is often called the TTL (through the lens) detector.

(d) Image display and recording

The output signals from the secondary electron detector are amplified and then transferred to the display unit. Since these scanning electron, appears on the monitor screen on the display unit, thus forming a SEM image. A cathode ray tube (CRT) was used for many years as a display unit; however in recent years, a liquid-crystal display (LCD) has been widely used probe can be changed in several steps. An extremely fast scan speed is used for observation and a slow scan speed is used for acquisition and a slow images.

To record an SEM image, in the past, the SEM image appearing on the CRT was photographed with a camera. But recently, the image has been recorded in a digital format (electronic file). This is because it is now difficult to get a high resolution CRT and there are many advantages of electronic filed. That is, it is easier to process images and convenient to send or receive image information. Note that an image format with 1Pa pixels is generally used for the electronic file.

(e) Vacuum system

This inside of the electron optical system and the specimen chamber must be kept at a high vacuum of 10^{-3} to 10^{-4} Pa. thus, these component are evaluated generally by a diffusion pump. If a user desires an oil-free environmental, a turbo molecular pump may be used. When a SEM incorporates an FE gun (a sputter ion pump is used because the FE gun needs an ultrathin high vacuum.

To exchange a specimen, either of two methods is applied one vents the entire specimen chamber at the time of specimen exchange. The other uses a specimen pre-evacuation chamber (air lock chamber) while keeping a high vacuum in the specimen chamber.

(f) Analysis of EDS

The energy dispersive x-ray spectrometer (EDS) is used to analyses characteristic x-ray spectra by measuring the energies of the x-rays. As shown on figure 2.5 when the x-ray emitted from the specimen enters the semiconductor detector, electron-holes pairs are generated whose quantities corresponds to the x-ray energy. Measuring these quantities (electric current) enables we to obtain the values of x-ray energy. The detector is coiled by liquid nitrogen, in order to reduce the

electric noise. The advantage of the EDS is that the x-ray from a wide range of elements from B and U are analyzed simultaneously.

X-ray spectra enable us to perform qualitative analysis the identification what elements are present in a specimen area irradiated with an electron beam. Three analyses is modes are available: point analysis to obtain a spectrum from a point irradiated with an electron beam, line analysis to display one-dimensional distribution of element of interest in a specified area. Mapping to display two-dimensional distributions of element of interest in a specified area. Mapping is often called “area analysis”. If the point analysis is applied to certain area (not a point), this qualitative analysis is performed while the electron probe is scanned. Over this area (an image is observed). The detection limit is different depending on the element. For EDS, this limit is a few thousand ppm.

2.6.3.2 Applications

The SEM plays a vital role in the following:

- ❖ It provides information about the structure of a specimen in the micrometer and the sub micrometer range. Imaging with secondary electrons enables a resolution down to the nanometer range.
- ❖ Typically backscattered electrons are to get images, where different gray levels in the image can be attributed to different chemical phases of a specimen.
- ❖ Electron backscattered diffraction enables both orientation imaging microscopy (OIM) and phase analysis. With a “false color representation” different region of a specimen’s surface can be allocated to different crystallographic orientations.
- ❖ Characteristic x-rays are always produced during the measurement process yield information about the chemical composition of the material. By using energy dispersive x-ray spectroscopy the quantification of elements from Boron to Uranium is possible.
- ❖ Similar to EDS wavelength dispersive x-ray spectroscopy yields information about the chemical composition of the material. As an advantage of this method the better energy resolution has to be emphasized, which helps to discern chemical elements, which cannot be identified with EDS.

2.6.4 High Resolution Transmission Electron Microscopy (HR-TEM)

Transmission Electron Microscopy (TEM) is a microscopy technique whereby a beam of electron is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electron 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 atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscopy. 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, nanotechnology, and semiconductor research [17].

2.6.4.1 Instrumentation

The instrumentation associated Transmission Electron Microscopy is outlined schematically in Figure 2.6. The apparatus of this wide instrument are as described below.

(a) Source formation

It may be a tungsten filament, or a lanthanum hexa boride (LaB6) source. LaB6 sources utilize small single crystals. By connecting this gun to a high voltage source (100-300 kV) the gun will given sufficient current, begin to emit electrons either by thermionic or field electron emission into the vacuum. This extraction is usually aided by the use of a Wehnelt cylinder. Once extracted, the upper lenses of the TEM allow for the formation of the electron probe to the desired size and location for later interaction with the sample. The interaction of electrons with a magnetic field will cause electrons to move according to the right hand rule, thus allowing for electromagnets to manipulate the electron beam.

(b) Optics

The lenses of a TEM allow for beam convergence, with the angle of convergence as a variable parameter, giving the TEM the ability to change magnification simply by modifying the amount of current that flows through the coil, quadrupole or hexapole lenses. Typically a TEM consists of three stages of lens. The stages are the condenser lenses, the objective lenses, and the projector lenses. The condenser lenses are responsible for primary beam formation, whilst the objective lenses focus the beam.

(c) Display

Imaging systems in a TEM consist of a phosphor screen, which may be made of fine (10-100 μm) particulate zinc sulphide, for direct observation by the operator. Optionally, an image recording system such as film based or doped YAG screen coupled CCDs.

(d) 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, and electrostatic plates to allow the operator to guide and manipulate the beam as required and Imaging devices.

(e) Vacuum system

To increase the mean free path of the electron gas interaction, a standard TEM is evacuated to low pressures, typically on the order of 10⁻⁴ Pa.

(f) 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 α . 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. 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, Φ is the work function and T is the temperature of the material. $J = AT^2 \exp\left(-\frac{\Phi}{KT}\right)$. 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 (LaB6) are required for the gun filament.

(g) Electron lens

Electron lenses are designed to act in a manner emulating that of an optical lens, by focusing parallel rays at some constant focal length. Lenses may operate electrostatically or magnetically. The majority of electron lenses for TEM utilise electromagnetic coils to generate a convex lens.

2.5.4.2 Applications

- ❖ Electron microscopy has led to the discovery of many new viruses, most notably the various viruses associated with gastroenteritis, for which it remained the principal diagnostic method until fairly recent times
- ❖ Both in the speed of diagnosis and the potential for detecting, by a single test, any viral pathogen or even multiple pathogens present within a sample.
- ❖ Electron microscopy has been used, however, to elucidate the structure and function of many bacterial features, such as flagellae, fimbriae and spores and in the study of bacteriophages.
- ❖ The important advantage of TEM over other characterization techniques is that information can be obtained both from real and reciprocal space.
- ❖ TEM techniques works with very high magnification only a small amount of material is required.

2.6.5 Raman Spectrometer (RS)

Raman spectroscopy is a highly specific non-destructive technique for molecular analytics. It can be used for routine qualitative and quantitative measurements of both inorganic and organic materials. The particular advantage of Raman spectroscopy is the possibility of measuring gases, vapor, aerosol, liquids and solids. The measurements condition can be room temperature observations, including in situ identification and quantification of combustion product in flames and plasmas. In the last few years, this technique has been recognized as a possible method for in situ planetary analysis. Raman spectroscopy is one of the few spectroscopic techniques available for both laboratory and remote measurements, the latter made at a distance from the sample by using optical fibers. Nowadays, Raman spectroscopy is becoming increasingly important as an analytical tool in conservation science. A growing number of renewed museums own a Raman instrument and some conservation scientists specialize in different application of this technique.

Raman spectroscopy treats the measurement of radiation scattered from a sample. Raman spectra are usually given as Wavenumber (cm^{-1}) shifts from the incident radiation. These shifts in wavenumbers are absolute energy difference between eigenstates of the molecule. Raman spectroscopy probes vibrational transition indirectly by light scattering. The Raman shifts have the same energy range as the infrared absorption, and in many cases the same absorption are observed. Thus Raman scattering can also be used for qualitative identification of organic compounds using group frequencies and scatter intensities. The selection rules of Raman scattering and infrared spectroscopy are different but the chemical information is similar.

The basic types of Raman instrument uncategorized are dispersive and non-dispersive Raman spectrometers. The dispersive system separates wavelength spatially, to be scanned across a single detector or monitored by many parallel detectors. The non-dispersive system does not separate different wave lengths spatially but usually modulates them so that each wavelength has a characteristic modulation frequency, the composite modulated signal is then monitored by a single detector and demodulated by a Fourier transform. While the non-dispersive systems are better for fluorescence avoidance, the dispersive systems have the advantages of higher sensitivity and better signal to noise ratio. However the major advantage is the lack of moving parts in the detection components of the system. These properties along with

fiber optic sampling makes dispersive system ideally suited for in situ measurements and today probable Raman instrument are mainly of the dispersive type.

The Raman spectroscopy is made with the advent of gas lasers and computers. The advantages of lasers are their high intensity, high monochromaticity, narrow band width, high resolution and coherence. From the time of invention of Raman Effect, both infrared and Raman spectra of chemical compounds have been effectively used for the determination of molecular structure and also for the quick identification of the presence of the characteristic group frequencies. In compound Raman spectroscopy, the sample is illuminated with a laser beam. Wavelengths close to the laser line (due to the Rayleigh scattering) are filtered out and the rest of the unfiltered light is dispersed onto a detector. Spontaneous Raman scattering is very weak compared to the Rayleigh scattering and separation of these two signals is necessary. Historically, Raman spectrometers used holographic diffraction gratings to achieve a high degree of laser rejection. However, modern instrumentation universally employs notch filters for laser rejection. Raman spectroscopy can be further applied for microscopic analysis of materials, such as polymers, ceramics and cells. This technique is known as Raman spectroscopy. Raman spectroscopy consists of a standard optical microscope, an excitation laser, a monochromator and a sensitive detector (such as CCD) [16].

2.6.5.1 Instrumentation

The instrumentation associated with laser Raman system is outlined schematically in Figure 2.7. The components of this generalized instrument are as described below.

(a) Source

The sources used in modern Raman spectroscopy are nearly always lasers because their high intensity is necessary to produce Raman scattering of sufficient intensity to be measured with a reasonable signal to noise ratio. Five of the most common lasers along with their wavelength (nm) used for Raman spectroscopy are; Argon (488 or 514.5nm), Krypton (530.9 or 647.1nm), Helium / Neon (632.8 nm), Diode laser (782 or 830nm) and Nd:YAG (1064nm). Because the intensity of Raman scattering varies as the fourth power of the frequency, argon and krypton sources that

emit in the blue and green region of the spectrum have an advantage over the other sources. Diode and Nd:YAG laser emit near-infrared radiation and are used as powerful excitation sources. Near-infrared sources have two major advantages over shorter wavelength lasers. The first is that they can be operated at much higher power (upto 50W) without causing photo decomposition of the sample. The second is that they are not energetic enough to populate a significant number of fluorescence producing excited electronic energy states in most molecules. Consequently, fluorescence is generally much less intense or nonexistent with these lasers. The Nd:YAG line at 1064 nm is particularly effective in eliminating fluorescence. The two line of the diode array laser at 782 and 830 nm also markedly reduce fluorescence in most cases. With the lower photon energy, a red or NIR laser may not promote the electronic transition (and hence the fluorescence) and so the Raman scatter may be far easier to detect. The cross-section for fluorescence is $\sim 10^{-16}$ cm² per molecule, but for Raman scattering, the value is between $10^{-31} \sim 10^{-26}$ cm² per molecule.

(b) Sample handing techniques

Sample handing techniques for Raman spectroscopic measurements is simpler than for infrared spectroscopy because glass used for windows, lenses and other optical components can be used instead of the more fragile and atmospherically less stable crystalline halides. In addition, the laser source is easily focused on a small sample area and the emitted radiation efficiently focused on slit. Consequently very small samples can be investigated. In fact, a common sample holder for non-absorbing liquid sample is a glass melting-point capillary.

❖ Liquid Samples

The spectrum of a liquid can be recorded as neat solution. Ordinarily about 0.3 ml of a liquid may be required. The sample could be taken in glass or silica containers or capillaries. The spectra can be measured directly from the reaction vessel. Water is a good solvent for recording the Raman spectra. Water absorbs strongly in the infrared but it is a poor Raman scatterer. Raman spectroscopy is thus a valuable tool for studying water soluble biological materials.

❖ *Solid Samples*

The Raman spectra of solids as polycrystalline material or as a single crystal can be recorded. No medium such as KBr or solvent is needed. A few milligrams of the solid samples are required. Solid can be packed into capillary tubes as a powder. The crystal can be mounted in a goniometer on a glass or silica fiber. The spectra can be measured for different orientation of the crystal. For single crystals, the Raman spectrum varies depending on the direction of the crystal axis, when polarized light is used as incident radiation. Raman spectra of adsorbed species can be recorded at different temperatures and pressures.

❖ *Gas Samples*

The Raman spectra of gases are generally weaker than those of liquids or solids and hence may require cells of larger path length. The gas may be filled in a glass or silica tube of 1 to 2 cm diameter. If the resolving power of the instrument is good and if the molecule has sufficiently low moment of inertia, the rotational fine structure may be observed on either side of the Rayleigh line. Generally a broadband contour may be observed. The main advantage of Raman spectroscopy is that it may be used for a wide variety of sizes and forms of the sample. Samples in gas, liquid and solid states can be examined easily.

(c) Filter

In any Raman configuration, a weak signal is observed in the presence of a much stronger Rayleigh scattering or different rejection occurring at the laser frequency. New filter designs based on holograph optic, either improve dielectric filter or semiconductor absorbers, can effectively reject the intense Rayleigh light. The rejection or notch filter is small and simple and permits the use of a small, single-stage spectrograph. Filters are placed between the source and the samples tube. Different filters are used for different excitation radiation. Filters made of quartz glass or nickel oxide glass is used for getting monochromatic radiations. The functions of filters are:

- To isolate a single exciting line
- To remove high-energy radiation that might cause photo decomposition or fluorescence.

- To remove the continuous spectrum in the region occupied by the Raman lines.
- Low noise signals and high sensitivity.

(d) Monochromators

In the monochromator, both lenses and mirrors have been used. Most Raman spectrometers use a diffraction grating as the dispersing element. A grating instrument has a wide aperture and a medium dispersion. A double monochromator is used to avoid stray light problem from scattering by dust particles in the sample.

(e) Detectors

Charge coupled device (CCD) detectors are part of the renaissance of Raman spectroscopy in 1986, and have replaced nearly all other detector configuration in dispersive Raman spectrometers used for chemical analysis. CCDs are based on storage and manipulation of electron and holes in a photosensitive semiconductor, usually silicon. The CCD surface is patterned with an array of electrodes; the basic event of importance to photo detections is the generation of an electron/hole pair in silicon by a photon of sufficient energy, each element forming an individual detector element called pixel. Photons in the 200 to 1100nm range generate photo electrons in the silicon with a probability that varies with the wavelength and determines the quantum efficiency curve. CCDs offer many advantages such as high sensitivity, low noise with improved signal to noise level and multichannel acquisition. The basic specification of CCDs is the two dimensional photoactive area. A common formation is 256×1024 square pixels with $25\mu\text{m}$ on each side. A term of importance in CCD detectors is the dark current, which is the spontaneous generation of the electron/holes pair unrelated to incident light intensity. This process is exponentially dependent with the temperature and CCDs must be cooled to reduced dark current. The temperature drop is achieved by liquid nitrogen, air cooling options or thermoelectric coolers.

2.6.5.2 Applications

- ❖ Raman spectroscopy now provides quick, easy, and most importantly, non-contact and non-destructive analysis, both qualitative and quantitative, with no sample preparation required. Samples may be tested directly with fiber probes or through glass, quartz, sapphire cells, and fibers.
- ❖ Raman is ideal for the studies of biological samples and chemical compounds in aqueous solutions, as water is only a weak Raman scattered and adds little interference.
- ❖ Raman can cover a broad range, $50 - 4000 \text{ cm}^{-1}$, in a single recording, which allows for characterization of both organic and inorganic compounds. In contrast, gratings, beam splitters, filters, and detectors must be changed to cover the same range by IR.
- ❖ Raman spectra are cleaner and sharper, and thus are more amenable to quantitative studies such as quantification of isolated Raman bands as well as qualitative studies such as database searching.
- ❖ As the diameter of the laser beam at its focal point is normally $0.2 - 2\text{mm}$, Raman spectra can be obtained with only a small quantity of sample. This is a great advantage over conventional IR. Furthermore, Raman microscope objectives can focus the laser beam down to $20 \mu\text{m}$ or even smaller, thus distinct small sample areas can be analyzed.
- ❖ Resonance Raman effects can be used to selectively enhance vibrations of a particular group in large biological molecules, where the intensities of Raman signals originating in this chromospheres can be selectively enhanced by a factor of 10^3 to 10^5 .

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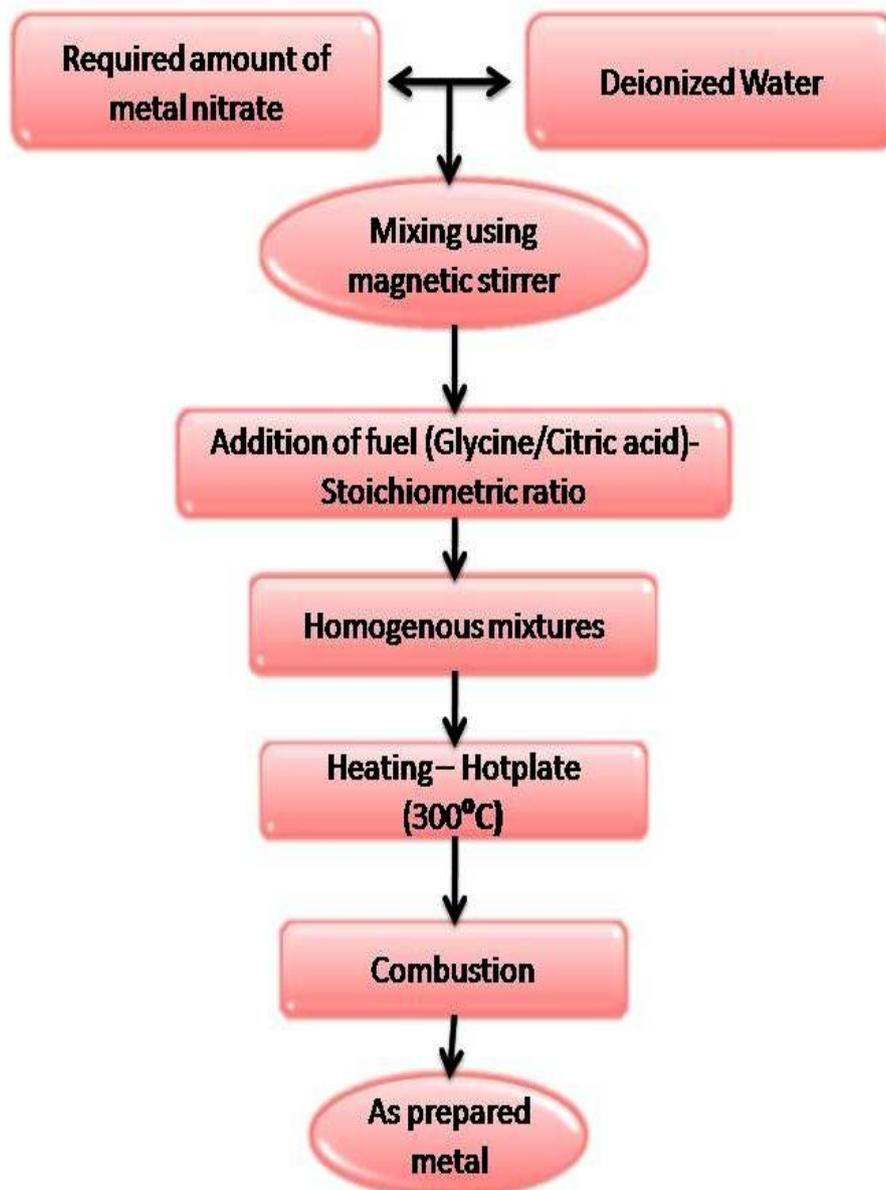


Figure.2.1. Schematic representation of the synthesis process.

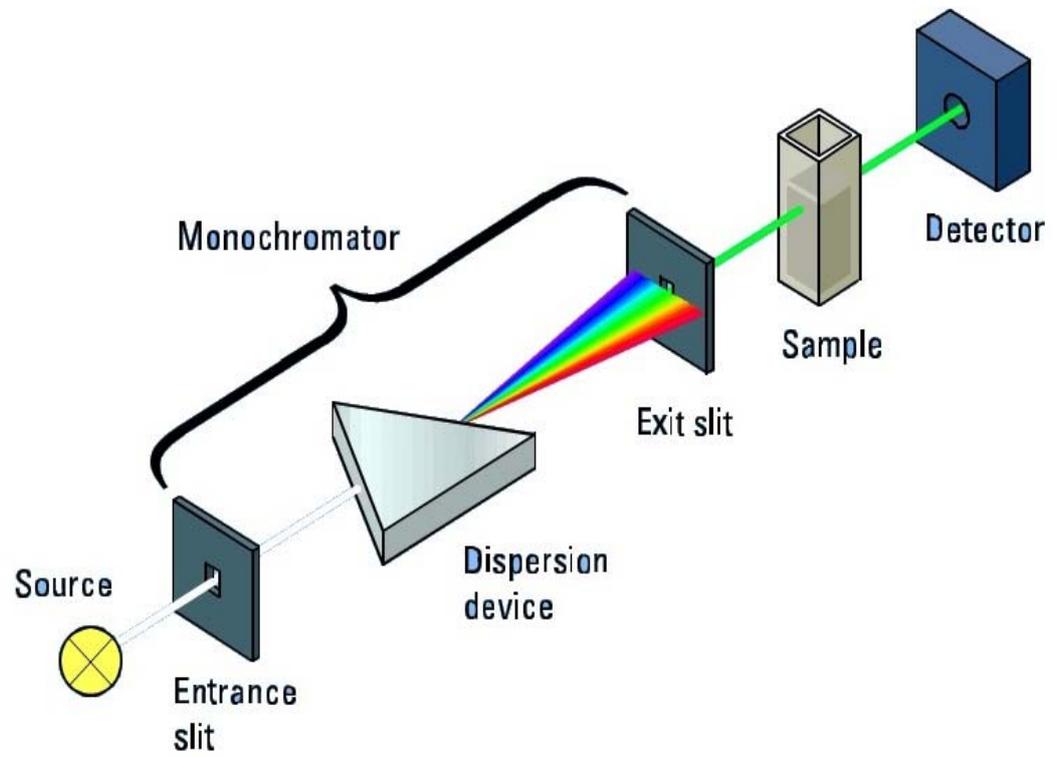


Figure 2.2 Schematic representation of instrument module of Ultraviolet spectroscopy

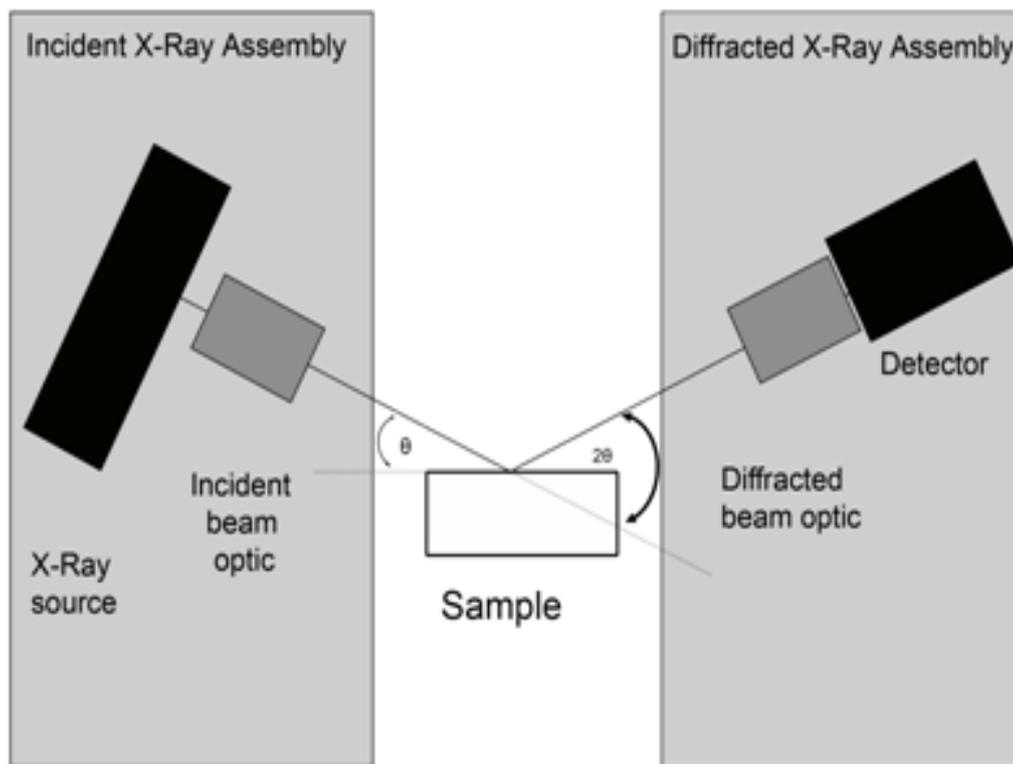


Figure 2.3 Schematic representation of XRD Instrumentation.

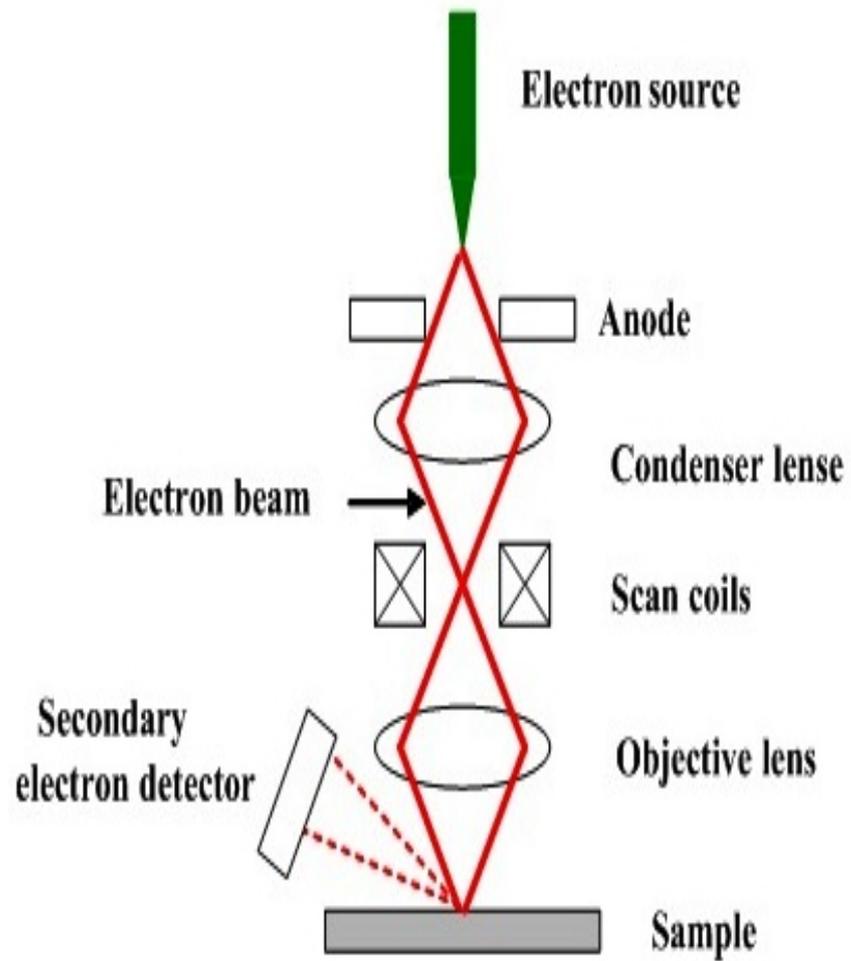


Figure 2.4 Schematic representation of SEM.

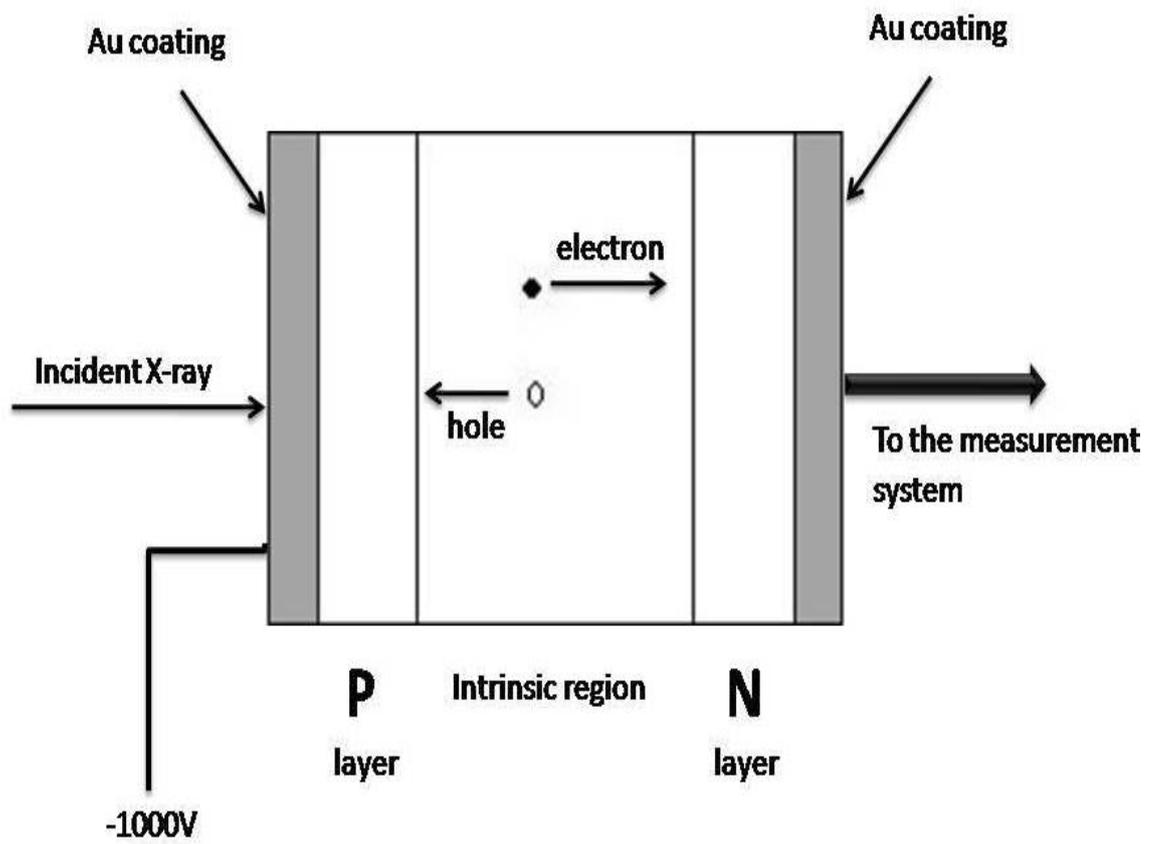


Figure 2.5 Schematic representation of EDS detector.

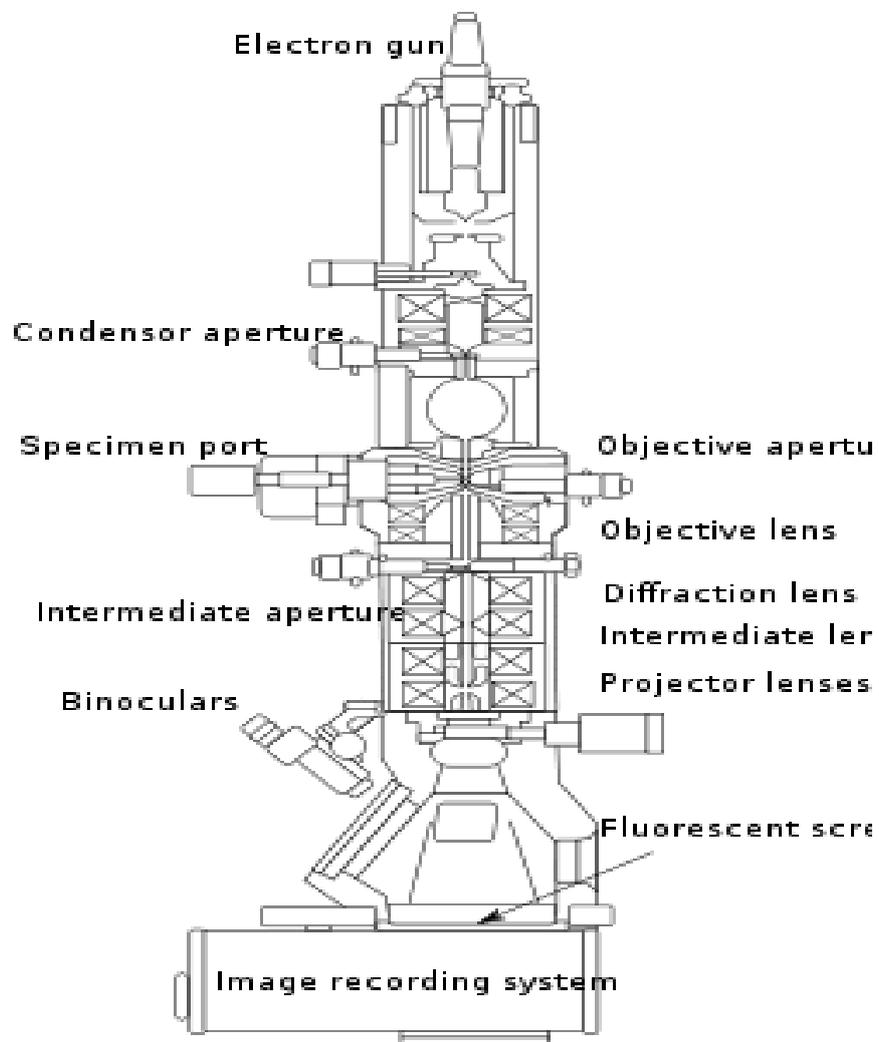


Figure 2.6 Schematic representation of TEM.

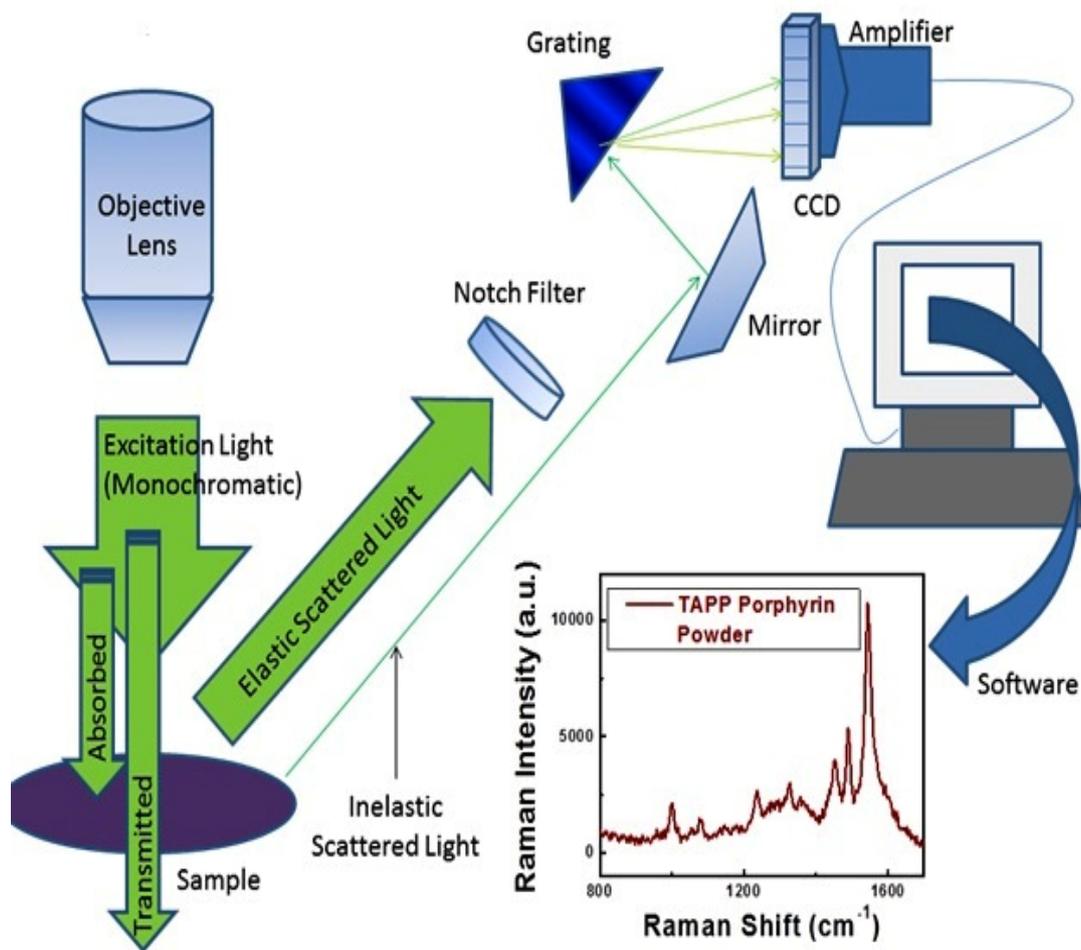


Figure 2.7 Schematic representation of a laser Raman system.