2.1 METHODS USED FOR THE SYNTHESIS OF NANOMATERIALS

The metal sulphide nanoparticles presented in this thesis have been prepared by following experimental techniques.

2.1.1 Hydrothermal synthesis: Hydrothermal synthesis is a widespread method used to synthesize nanostructures. This method makes use of the solubility of almost all inorganic substances in water at elevated temperatures and pressures and subsequent crystallization of the dissolved material from the fluid. Water at elevated temperatures plays an essential role in the precursor material transformation because the vapour pressure is much higher and the structure of water at elevated temperatures is different from that at room temperature. The properties of the reactants, including their solubility and reactivity, also change at high temperature. The changes mentioned above provide more parameters to produce different high-quality nanoparticles and nanotubes, which are not possible at low temperatures. During the synthesis of nanocrystals, parameters such as water pressure, temperature, reaction time, and the respective precursor-product system can be tuned to maintain a high simultaneous nucleation rate and good size distribution. Different types of oxides and sulphides nanoparticles such as TiO₂, LaCrO₃, ZrO₂, BaTiO₃, SrTiO₃, Y₂Si₂O₇, Sb₂S₃, CrN, α-SnS₂, PbS, and SnS₂ nanotubes, Bi₂S₃ nanorods, and SiC nanowires have been successfully synthesized in this way. The solvent is not limited to water but also includes other polar or nonpolar solvents and the process is more appropriately called solvothermal synthesis in different solvents.

2.1.2 Chemical precipitation/Co-precipitation method: Co-precipitation is a very simple and inexpensive method for the synthesis of nanoparticles. During the synthesis of inorganic nanoparticles by chemical precipitation method, the kinetics of nucleation and particle growth in homogeneous solutions can be adjusted by the controlled release of anions and cations. Careful control of precipitation kinetics can result in monodisperse nanoparticles. Once the solution reaches a critical supersaturation of the species forming particles, only one burst of nuclei occurs. Thus, it is essential to control the factors that determine the precipitation process, such as the pH and the concentration of the reactants and ions. The particle size is influenced by the reactant concentration, pH, and temperature. By engineering these factors, nanoparticles with narrow size distributions have been produced. Although the method of using precipitation to prepare nanoparticles is very easy and simple, very
complicated nanostructures including core-shell structures can also be constructed using this method [147].

2.1.3 Sonochemical Method

The utilization of ultrasonic irradiation for the production of nanomaterials is a topic of great interest. This is a consequence of the simplicity of the sonochemical method, inexpensive price of the equipment and in many cases the as prepared material is obtained in crystalline phase. The chemical effects of ultrasound come from non-linear acoustic phenomenon, primarily acoustic cavitation. This can be divided into three stages: (i) formation (ii) growth and (iii) implosive collapse of bubbles [148]. Once a bubble is formed, it can grow as dissolved gas molecules enter during the expansion phase of sound waves and shrinks during the compression phase. Thus, the bubbles grow slowly over many acoustic cycles. In strong acoustic fields, the implosive collapse of the bubbles generates a localized hotspot through adiabatic compression or shock wave formation within the gas phase of the bubble. The extreme conditions obtained during bubble collapse have been exploited to generate metal nanoparticles [149-151]. An ultrasonic bath (Sonic make) equipped with standard probe made of Titanium alloy Ti-6 Al-4V operating at 20 kHz with a maximum output of 130 W was used for the ultrasonic irradiation for synthesizing nanoparticles.

2.2 EXPERIMENTAL TECHNIQUES

2.2.1 Reaction Autoclaves

PTFE (polytetrafluoroethylene) lined acid digestion bombs purchased from Parr Instrument Company (Illinois, USA) were used as reaction autoclaves. PTFE is used for lining these acid digestion bombs since Teflon is an inert material. The maximum operating temperature is 180 °C and the maximum pressure is 650 psi for the autoclaves which were used in our experiments.

The pressure generated within these bombs is highly dependent on the nature of the materials, the filling level and the amount of heat applied to promote the reaction. If the bomb is heated above its maximum temperature limit, the vapour pressure of the materials in the bomb increases exponentially with temperature and the strength of the materials from which the bomb is made fall off again exponentially. When a water based solution is heated to 250 °C, it expands to fill a space approximately 25% larger than its standard state volume. If there is not sufficient vapour space in the bomb to accommodate this expansion, tremendous hydrostatic pressure will destroy the bomb.
Most inorganic digestions proceed smoothly without unusual hazards, using not more than 1.0 gram of sample in a 23 mL bomb. The bomb must never be completely filled as there must always be vapour space above the surface of the charge. The total volume of the charge must never exceed 66% of the capacity of the cup when working with inorganic materials.

Many organic materials may be treated satisfactorily in these digestion bombs with careful attentions. In all cases the sample size and the amount of oxidant must be carefully controlled. The dry weight of organic matter must not exceed 0.1 gram in a 23 mL bomb. In all operations the temperature and the pressure must be held within prescribed limits.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>106</td>
<td>305</td>
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<tr>
<td>155</td>
<td>705</td>
</tr>
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<td>162</td>
<td>765</td>
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<td>221</td>
<td>1670</td>
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<td>236</td>
<td>1960</td>
</tr>
<tr>
<td>258</td>
<td>2505</td>
</tr>
</tbody>
</table>

Table 1 Pressure developed at constant volume by 10 mL of aqua regia in a 23 mL space (Source: Parr company)

Highly exothermic reactions or other reactions which may be expected to release large volumes of gas should be avoided (Parr Company 1999). Perchloric acid should not be used in these bombs due to its unpredictable behaviour when heated in a closed vessel. Parr metal-jacketed acid digestion bombs can be heated in ovens or block heaters. At the end of a run, the bomb must be cooled to the touch before removing the PTFE cup. Cooling must proceed slowly and naturally.

In our laboratory 23 mL Teflon lined acid digestion bombs (Parr Instruments, model 4749) were used as reaction autoclaves. Schematic representation of model 4749 is shown in Figure 2.1. The sample and the digestion media were added to the Teflon cup. After adding, the Teflon cup was placed into the bomb body. Then, the corrosion disc (thinner, next to the Teflon cover) and the rupture disc (thicker, on the outside of the sandwich) were placed on top of the liner. After that, the spring with
upper and lower pressure plates was added. After adding the spring, the screw cap was attached and turned down firmly by hand. The bomb was placed into an oven and heated for specific time at specific temperature. Finally, the autoclave was allowed to cool in the oven.

![PTFE cup with cover, acid digestion bomb body, screw cap, pressure plate (upper), pressure plate (lower), corrosion and rupture discs, spring](image)

**Fig. 2.1** PTFE cup with cover, acid digestion bomb body, screw cap, pressure plate (upper), pressure plate (lower), corrosion and rupture discs, spring (from left to right).

After the cooling step, the obtained product was washed several times with different solvents in order to remove the unreacted materials. The obtained nanomaterials were preserved for further analysis.

### 2.2.2 Spectral and other techniques

(a) **Infrared Spectra**

The FTIR spectra of the nanoparticles were recorded on Perkin Elmer RX-1 FTIR spectrophotometer using KBr discs in the range 4000-400 cm⁻¹.

(b) **Scanning electron microscopy (SEM)**

The surface morphology was analyzed by a JEOL T-300 digital scanning electron microscope accelerating at a voltage of 10 KV and at different magnifications.

(c) **Transmission electron microscopy (TEM)**

Transmission electron micrographs (TEM) were collected on TECNAI 200 Kv TEM (Fei, Electron Optics).
Preparation and characterization of some transition and inner transition metal-sulphide nanoparticles

2.3 PRINCIPLES UNDERLYING VARIOUS PHYSICO-CHEMICAL TECHNIQUES

2.3.1 Powder X-Ray diffraction method (PXRD)

X-ray diffraction (XRD) is an analytical technique based on X-ray scattering from crystalline materials. It is mostly used for phase identification of a crystalline material and can provide information on unit cell dimensions. The powder pattern is considered as a characteristic “fingerprint” of a phase as the positions of the peaks in a powder pattern are determined by the size, shape, and symmetry of the unit cell and the peak intensities are determined by the arrangement of atoms within the cell. In a mixture of phases, the diffraction patterns overlap (but do not otherwise interfere), so it is possible to identify the components of a mixture. Each material produces a unique X-ray "fingerprint" of X-ray intensity versus scattering angle that is characteristic of its crystalline atomic structure. Qualitative analysis is possible by comparing the XRD pattern of an unknown material to a library of known patterns. The exact nature of X-rays was not known at the time of their discovery in 1895 by Wilhelm Conrad Rontgen. The question posed at the time was "are X-rays particles or are they waves like visible light?" Showing that X-rays could diffract would prove...
that X-rays have a wave-like nature. Diffraction effects are observed only when the repeat distances in a material are of the order of magnitude of the wavelength of the radiation. At that time it was strongly believed that crystals were made up of many repeating blocks and that each repeating block contained a constant number of the same type of atoms. From some simple calculations using density, atomic numbers, and Avogadro's number, researchers of the time were able to show that simple crystals should have repeating units of the size needed for their proof of the wave-like nature of X-rays. Friedrich and Knipping performed the first X-ray diffraction experiment using a crystal of copper sulphate. They obtained a diffraction pattern and concluded that X-rays must be electromagnetic radiation. Bragg diffraction was first proposed by William Lawrence Bragg in 1912 as a means of analyzing the structure of crystals. Bragg and his father William Henry Bragg collimated X-rays to diffract off from different crystal planes. The X-rays were then collected in an ionization chamber and the level of ionization was measured as a function of the incident angle of the X-rays. Using this method, the Braggs were able to determine the crystalline spacing for a number of substances. W. L. Bragg recognized a predictable relationship among several factors.

1. The distance between similar atomic planes in a mineral (the interatomic spacing) which we call the d-spacing and measure in angstroms.

2. The angle of diffraction which we call the theta angle and measure in degrees. For practical reasons the diffractometer measures an angle twice that of the theta angle. Not surprisingly, we call the measured angle ‘2-theta’.

3. The wavelength of the incident X-radiation, symbolized by the Greek letter lambda

\[ n\lambda = 2d \sin \theta \]

In 1919 A. W. Hull gave a paper titled, “A New Method of Chemical Analysis.” Here he pointed out that “…every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independent of the others.”

A powder X-ray diffractometer consists of X-ray source (usually X-ray tube), a sample stage, a detector and a way to vary angle \( \theta \). The X-ray is focused on the sample at some angle \( \theta \), while the detector opposite the source reads the intensity of
the X-ray, it receives at $2\theta$ away from the source path. The incident angle is then increased over time while the detector angle always remains $2\theta$ above the source path.

![Principle underlying the powder x-ray diffractometer](image)

**Fig. 2.2** Principle underlying the powder x-ray diffractometer

When an X-ray beam hits an atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. In almost all directions, we will have destructive interference, that is, the combining waves are out of phase and there is no resultant energy leaving the solid sample. However, the atoms in a crystal are arranged in a regular pattern, and in a very few directions, we will have constructive interference. The waves will be in phase and there will be well defined X-ray beams leaving the sample at various directions. Hence, a diffracted beam may be described as a beam composed of a large number of scattered rays mutually reinforcing one another. This model is complex to handle mathematically, and in day to day work we talk about X-ray reflections from a series of parallel planes inside the crystal. In X-ray powder diffractometry, X-rays are generated within a sealed tube that is under vacuum. A current is applied that heats a filament within the tube: Higher the current, greater the number of electrons emitted from the filament. This generation of electrons is analogous to the production of electrons in a television picture tube. A high voltage, typically 15-60 Kilovolts is applied within the tube. This high voltage accelerates the electrons, which then hit a target. Copper is the most common target material for single-crystal diffraction, with CuK$_\alpha$ radiation = 1.5418 Å. When these electrons hit the target, X-rays are produced. The wavelength of these X-rays is characteristic of that target. These X-rays are collimated and directed onto the sample, which has been ground to a fine powder (typically to produce particle sizes of less than 10 microns). A detector detects the X-ray signal. The signal is then
processed either by a microprocessor or electronically, converting the signal to a count rate. Changing the angle between the X-ray source, the sample, and the detector at a controlled rate between preset limits is an X-ray scan. When an X-ray beam hits a sample and is diffracted, we can measure the distances between the planes of the atoms constituting the sample by applying Bragg's Law.

Bragg's Law is \( n\lambda = 2d \sin\theta \),

where the integer \( n \) is the order of the diffracted beam, \( \lambda \) is the wavelength of the incident X-ray beam, \( d \) is the distance between adjacent planes of atoms (the \textit{d}-spacings), and \( \theta \) is the angle of incidence of the X-ray beam.

Since the value of \( \lambda \) is known and that of \( \theta \) can be measured and hence \textit{d}-spacings can be calculated. The \( \lambda \) and \( d \) are measured in the same units, usually angstroms. However, the intensities of the reflections are determined by the distribution of the electrons in the unit cell. The highest electron density is found around atoms. Therefore, the intensities depend on what kind of atoms we have and where in the unit cell they are located. Planes going through areas with high electron density will reflect strongly, planes with low electron density will give weak intensities. The geometry of an XRD unit is designed to accommodate this measurement. The characteristic set of \textit{d}-spacings generated in a typical X-ray scan provides a unique "fingerprint" of the mineral or minerals present in the sample. When properly interpreted, by comparison with standard reference patterns and measurements, this "fingerprint" allows for identification of the material.

**Calculation of crystallite size from XRD by using Williamson-Hall method**

It relies on the principle that the approximate formulae for size-broadening and strain-broadening vary quite differently with respect to Bragg angle, \( \theta \). Strain-induced broadening arising from crystal imperfections and distortions are related by \( \varepsilon \approx \beta_s / \tan \theta \). The W-H method does not follow a \( 1/\cos \theta \) dependency as in the Scherrer equation but instead varies with \( \tan \theta \). This fundamental difference allows for a separation of reflection broadening when both microstructural causes (small crystallite size and microstrain) occur together. The different approaches presented in the following assume that size and strain broadening are additive components of the total integral breadth of a Bragg peak. The distinct \( \theta \) dependence of both effects laid the basis for the separation of size and strain broadening in the analysis of Williamson and Hall. Addition of the Scherrer equation and \( \varepsilon \approx \beta_s / \tan \theta \) results in following equations:
\[ \beta_{hkl} = \beta_S + \beta_D \]
\[ \beta_{hkl} = (k \lambda/D \cos\theta) + (4\varepsilon \tan\theta) \]
Rearranging Eq. gives:
\[ \beta_{hkl} \cos\theta = (K \lambda/D) + (4\varepsilon \sin\theta) \]

The above equations are W-H equations. A plot is drawn with \(4\sin\theta\) along the x-axis and \(\beta_{hkl} \cos\theta\) along the y-axis for as-prepared nanoparticles. From the linear fit to the data, the crystalline size is estimated from the y-intercept, and the strain \(\varepsilon\), from the slope of the fit.

2.3.2 Infrared Spectroscopy

Infrared spectroscopy is one of the most powerful analytical techniques, which offers the possibility of chemical identification. One of the most important advantages of IR spectroscopy over the other usual methods of structural analysis is that it provides useful information about the structure of molecule quickly without tiresome evaluation methods. The technique is based upon the simple fact that a chemical substance shows marked selective absorption in the IR region. An IR spectrum of a chemical substance is a fingerprint for its identifications.

The basic theory of vibrational spectra involves knowledge of:

a) Dipole moment
b) Vibrations of diatomic molecules
c) Beer-Lambert’s law
d) Vibrations of polyatomic molecules and selection rules
e) Symmetry properties and point groups
f) Classification of normal vibrations in each species

A large number of absorption bands are observed in the IR region due to the excitation of molecular vibrations and rotations. The absorption of IR radiations causes the various bonds in a molecule to stretch and bend with respect to one another. The nature of peaks obtained in the spectrum depend on the arrangement of atoms in space, their masses, bond lengths, bond angles and the force between the atoms. When radiations with frequency range less than 100 cm\(^{-1}\) are absorbed, molecular rotation takes place in the substance and discrete lines are formed in the spectrum. Molecular vibrations are set in, when more energetic radiation in the region \(10^4\) to \(10^2\) cm\(^{-1}\) are passed through the sample of the substance. As a single vibrational energy change is accompanied by a large number of rotational energy changes, so the
vibrational spectra appear as vibrational-rotational bands. The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule. The sharply defined frequencies of these vibrations fall within the IR region of the electromagnetic spectrum. The most useful range for general problem solving lies between 4000 and 400 cm$^{-1}$, the mid IR range. Interpretation of the IR spectrum stems from the fact that the structural features of the molecule or functional groups attached to the molecules produce characteristic and reproducible absorptions in the spectrum [152,153].

The fundamental vibrational frequency of a molecule can be stated by Hooke’s law as:

$$\nu = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2}$$

where $\nu$ = Fundamental vibration frequency, s$^{-1}$

$k$ = Force constant and

$\mu$ = reduced mass

This simple equation provides a link between the strength of the covalent bond between two atoms, the masses of the interacting atoms and the frequency of vibration. Although simple in concept, there is a reasonably good fit between the bond stretching vibrations predicted and the values observed for the fundamentals. But this simple model does not account for repulsion and attraction of electron cloud at the extremes of the vibration and does not accommodate the concept of bond dissociation at high levels of absorbed energy.

In a complex compound, an additional bond is formed between the metal and the ligand, so there is a slight change in bond lengths, angles and interatomic forces within the ligands. The spectra of complex compounds in different regions have been studied and it has been observed that the vibrations due to ligands are usually found in high wave number (4000 - 650 cm$^{-1}$) and vibrations due to co-ordinate bonds are found in the low wave number region (650 - 50 cm$^{-1}$). The spectrum of a free ligand and its complex are different due to

i) Change in band position

ii) Change in relative band intensities along with the appearance of new bands, mostly weak bands
iii) Single band in the free ligand may split into several closely spaced bands in the complex.

From the observations of infrared spectra of a number of compounds having a common group of atoms, it has been found that regardless of the rest of the molecules, this common group absorbs light energy over a narrow range of frequencies, called the ‘group frequencies’. These group frequencies for a number of organic and inorganic compounds have been summarized as group frequencies chart, which are highly useful in the identification of the atomic group as observed from the different infrared spectra [154,155]. In order to characterize compounds, an infrared spectrum is run through an examination of large number of spectra of known compounds to correlate specific vibrational absorption maxima with the atomic groupings responsible for the absorption. Such correlations provide a powerful tool for the identification of a covalent compound.

2.3.3 Electronic Spectroscopy

Absorption spectroscopy refers to spectroscopic techniques that measure the absorption of radiation, as a function of frequency or wavelength, due to its interaction with a sample. The sample absorbs energy, i.e., photons, from the radiating field. The intensity of the absorption varies as a function of frequency, and this variation is the absorption spectrum. Absorption spectroscopy is performed across the electromagnetic spectrum. Absorption spectroscopy is also employed in studies of molecular and atomic physics, astronomical spectroscopy and remote sensing.

The variety of colors in inorganic chemistry has long been fascinating the observer. The color of the compounds arises from electronic transitions between levels whose spacing corresponds to the wavelengths available in visible light. In complexes, these transitions are frequently referred to as d-d transitions because they involve metal centred molecular orbitals in which the excitations of electrons occur. The colors produced are intimately related to the magnitude of the spacing between these levels. The spacing depends on various factors such as geometry of the complex, the oxidation state of the central metal atom, the nature of the ligands present. The electronic spectra of complexes can, thus, provide valuable information related to bonding and structure.

Any molecular system possesses three types of energy namely electronic \( (E_{ele}) \), vibrational \( (E_{vib}) \) and rotational \( (E_{rot}) \) with decreasing magnitude in same order for a
system. Absorption of energy leads to transition of electron from ground state to excited state. The absorption band, thus, obtained is broad, smooth and never very sharp due to the fact that the electronic absorption is accompanied with a corresponding change in the vibrational and rotational energies as well. The relationship between the energy absorbed in an electronic transition and the frequency, $\nu$, wavelength, $\lambda$ and wave number, $\bar{\nu}$, of the radiation producing the transition is

$$\Delta E = h\nu = hc/\lambda = h.\bar{\nu}.c$$

where, $h$ is Planck’s constant, $c$ is the velocity of light and $\Delta E$ is the energy absorbed in an electronic transition in a molecule from a low-energy state (ground state) to a high state (excited state). The position of absorption maxima for a molecule depends on the difference in the energy of the ground state level to that of excited state; larger the difference between the energies, higher is the frequency of absorption and thus, smaller will be the wavelength. Absorption band shows two important characteristics; position of the band which depends on the energy difference between electronic level and intensity which depends on the interaction between the radiation and electronic system as well as on the energy difference between the ground and excited state.

While color in inorganic compounds is generally associated with the presence of a partially filled d shell, there are many such compounds with $d^0$ or $d^{10}$ configurations, which are intensely colored. Mercury (II) iodide (brick red, $d^{10}$), the manganate (VII) ion (purple, $d^0$), bismuth (III) iodide (orange red, $d^{10}s^2$) and lead iodide (yellow, $d^{10}s^2$) are common examples. In such cases color arises, at least in part, as a consequence of light absorption due to transfer of an electron from an orbital primarily on the ligand, to one primarily on the metal or vice-versa. Such charge or electron transfer processes are termed ‘Ligand to Metal charge transfer’, LMCT, and ‘Metal to Ligand charge transfer’, MLCT, respectively. Such a process is not confined to $d^0$ and $d^{10}$ species and occurs frequently in transition metal complexes.

The most straightforward approach to absorption spectroscopy is to generate radiation with a source, measure a reference spectrum of that radiation with a detector and then re-measure the sample spectrum after placing the material of interest in between the source and detector. The two measured spectra can then be combined to determine absorption spectrum of material. The sample spectrum alone is not sufficient to determine the absorption spectrum because it will be affected by the
experimental conditions- the spectrum of the source, the absorption spectra of other materials in between the source and detector and the wavelength dependent characteristics of the detector. The reference spectrum will be affected in the same way, though, by these experimental conditions and therefore the combination yields the absorption spectrum of the material alone.

**Fig. 2.3** Figure illustrating the working principle of a UV spectrophotometer

### 2.3.4 Scanning Electron microscopy

Scanning electron microscopy (SEM) is one of the most versatile and widely used tools of modern science as it allows the study of both morphology and composition of biological and physical materials. SEM is an incredible tool for seeing the unseen worlds of microspace. This is one of the widely used instruments in material research laboratories. Conventional light microscopes use a series of glass lenses to bend light waves and create a magnified image. The SEM creates the magnified images by using electrons instead of light waves. However, since electrons are excited to high energy (keV), so wavelength of electron waves is quite small and resolution is quite high. SEM shows very detailed 3-D images at much higher magnification than is possible with light microscope. In addition to this, it also provides useful information about the external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a two-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 micron in width can...
be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analysis of selected point locations on the sample and provide the following information.

1) acquiring elemental maps or spot chemical analysis using EDS (Energy dispersive spectroscopy),
2) discrimination of phases based on mean atomic number (commonly related to relative density) using BSE (Backscattered electrons), and
3) compositional maps based on differences in trace element activators (typically transition metal and Rare Earth elements) using CL (Cathodoluminescence).

In a typical SEM, electrons are thermionically emitted from a tungsten or lanthanum hexaboride (LaB₆) cathode and are accelerated towards an anode; alternatively, electrons can be emitted via field emission (FE). The electron beam, which typically has an energy ranging from a few hundred eV to 100 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 1 to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam horizontally and vertically so that it scans in a faster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The size of the interaction volume depends on the beam accelerating voltage, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and sample, results in emission of electrons along with electromagnetic radiations (X-rays) which can be detected to produce an image.
**Fig. 2.4** Schematic representation of a scanning electron microscope

The emitted electrons in SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals. 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. The most common imaging mode monitors low energy (<50 eV) secondary electrons. Due to their low energy, these electrons originate within a few nanometers from the surface. The electrons are detected by a scintillator-photomultiplier device and the resulting signal is rendered into a two-dimensional intensity distribution that can be viewed and saved as a Digital image. The brightness of the signal depends on the number of secondary electrons reaching the detector. If the beam enters the sample perpendicular to the surface, then the activated region is uniform about the axis of the beam and a certain number of electrons "escape" from within the sample. As the angle of incidence increases, the "escape" distance of one side of the beam will decrease, and more secondary electrons will be emitted. Thus, steep surfaces and edges tend to
be brighter than flat surfaces, which results in images with a well-defined, three-dimensional appearance. Using this technique, resolutions of 1 nm are possible.

Backscattered electrons (BSE) consist of high-energy electrons originating in the electron beam that are reflected or back-scattered out of the specimen interaction volume. Backscattered electrons may be used to detect contrast between areas with different chemical compositions, especially when the average atomic number of the various regions is different, since the brightness of the BSE image tends to increase with the atomic number. Backscattered electrons can also be used to form electron backscatter diffraction (EBSD) image. This image can be used to determine the crystallographic structure of the specimen.

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 (that is related to the difference in energy levels of electrons in different shells for a given element). 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.

2.3.5 Transmission electron microscopy

An electron and an optical microscope work on a similar principle, though they have vastly different resolving powers, because of different radiation source used. The radiation either photon or electron falls on the condenser lens, which focuses the beam onto the specimen. The use of this technique in the morphological and structural aspect of material science is of great importance. Micro-structural analysis in terms of defects and pinning and information on the grain boundaries through high-resolution imaging can be performed. In addition using the selected area electron diffraction (SAED), structural information can be obtained. The first TEM was built by Max Knoll and Ernst Ruska in 1931, with this group developing the first TEM with resolution greater than that of light in 1933 and the first commercial TEM in 1939.

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 thousands of 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, nanotechnology, and semiconductor research.

The imaging system in the TEM consists of an objective lens, projector lens, and fluorescence screen. The objective lens focuses the beam after it has traversed through the specimen, and forms an intermediate image. This intermediate image is magnified by a projector lens to form a magnified final image. In an optical microscope the lenses are made up of glass and have fixed focal lengths. However, in the TEM, electromagnetic lenses used consist of ferromagnets and copper coils. The focal length of the electromagnetic lenses in the TEM can be changed by varying the current through the coil. An electron beam instead of a photon (light beam) is used for the image formation in TEM. Due to the short wavelength of electrons TEM can provide a resolution far better than optical microscopes. A schematic diagram of a Transmission Electron Microscope (TEM) is shown in figure 2.5.

The transmission electron microscope (TEM) uses a high voltage electron beam to create an image. The electron beam is produced by an electron gun, commonly fitted with a tungsten filament cathode as the electron source. The electron beam is accelerated by an anode typically at +100 keV (40 to 400 keV) with respect to cathode focused by electrostatic and electromagnetic lenses, and transmitted through an ultrathin specimen that is in part transparent to electrons and in part scatters them out of beam. When it emerges from the specimen, the electron beam carries information about the structure of the specimen that is magnified by the objective lens system of the microscope. The spatial variation in this information (the image) may be viewed by projecting the magnified electron image onto a fluorescent viewing screen coated with a phosphor or scintillator material such as zinc sulphide. Alternatively, the image can be photographically recorded by exposing a photographic film or plate directly to electron beam or a high resolution phosphor may be coupled by means of a lens optical system or a fibre optic light guide to the sensor of a CCD (charge-coupled device) camera. The image detected by the CCD may be displayed on a monitor or computer.

Resolution of TEM is limited primarily by spherical aberration, but a new generation of aberration correctors have been able to partially overcome spherical aberration to increase resolution. Hardware correction of spherical aberration for the
high resolution transmission electron microscopy (HRTEM) has allowed the production of images with resolution 0.5 Å (50 picometers) and magnifications above 50 million times. The ability to determine the position of atoms within materials has made the HRTEM, an important tool for nano-technology research and development.

**Fig. 2.5** Schematic representation of a transmission electron microscope

(a) diffraction mode (b) image mode

### 2.3.6 Selected area electron diffraction (SAED)

Selected area electron diffraction (SAED) is a TEM technique to obtain diffraction patterns that result from the electron beam scattered by the sample lattice. Obeying the Bragg’s law, the electrons are scattered elastically by the lattice, therefore, we can index the diffraction spots in the pattern and identify the phases in the sample and study their structures. Typically, the area size of the sample been selected by SAD aperture is 0.5-1 μm, so the microstructure of the sample could be fine selected and tested.

From a SAED pattern, the material scientists can obtain structural information of the sample, like crystalline symmetry, unit cell parameter and space group etc. While the metallurgists can learn the information about phase separation, texture, precipitation and some other microstructure features in their samples.

The SAED test is one of the most conventional experiments that are conducted by TEM. Almost all the TEM machines with a parallel electron beam source are
capable of SAED tests. The world-famous TEM machine producers are listed as follows: Zeiss, FEI/Philips, JEOL and Hitachi. The SAED technique in TEM test is a powerful tool for material characterization. Its capability includes identification of the material species, determination of unit cell parameters etc.

To analyze the SAED patterns, we combine the Bragg's equation and geometric relationship in the reciprocal space,

\[ 2d \sin \theta = \lambda \]  \hspace{1cm} \text{(Bragg's law)}

\[ \tan 2\theta = \frac{D}{L} \]  \hspace{1cm} \text{(geometric relationship in reciprocal space)}

where \( d \) is spacing between planes, \( \lambda \) is the wavelength of the electron beam, \( \theta \) is the diffraction angle, \( D \) is the distance between spots on the SAED pattern, \( L \) is camera length for the TEM machine. For a very small diffraction angle \( \theta \), \( 2\sin \theta \) equals to \( \tan 2\theta \), therefore, we can calculate the \( d \)-spacings for the spots on the SAD pattern by

\[ d = \frac{D}{(\lambda L)} \]

Every spot in the SAED pattern corresponds to lattice planes of a certain miller index in single crystal. All the spots on the pattern could be indexed. Every ring in SAD pattern corresponds to a group of lattice planes of the same miller index family in the polycrystalline sample. If we fix the electron beam and rotate the sample, some spot/ring will be activated, other spot /ring may die away, all of which is based on the diffraction condition stated above.

Typically, a pattern of diffraction spots results from the electron beam diffracted by a single crystal, while the sample containing large number of small randomly distributed grains results in continuous rings. That is because these grains all contribute to the formation of the diffraction pattern. The radii of the rings are inversely proportional to the interplanar spacings \( d_{hkl} \) of a lattice plane of crystals, which obeys the relationship that mentioned above:

\[ d = \frac{D}{(\lambda L)} \]

The rings turn from continuous to dotty as the grain size of the polycrystalline material increases. When it comes to the case that the grain size is extremely small or the material is totally amorphous, the feature of concentric rings disappears but only left a halo around the bright spot in the center, which indicates that the electrons are diffracted randomly by the material of amorphous structure.

2.3.7 Energy Dispersive spectroscopy (EDS)

Energy dispersive spectroscopy (EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. As
a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from each other.

To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or protons or a beam of X-rays is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

Four primary components of the EDS setup are

1. the excitation source (electron beam or x-ray beam)
2. the X-ray detector
3. the pulse processor
4. the analyzer.

Electron beam excitation is used in electron microscopes, scanning electron microscopes (SEM) and scanning transmission electron microscopes (STEM). X-ray beam excitation is used in X-ray fluorescence (XRF) spectrometers. A detector is used to convert X-ray energy into voltage signals; this information is sent to a pulse processor, which measures the signals and passes them onto an analyzer for data display and analysis. The most common detector now is Si(Li) detector cooled to cryogenic temperatures with liquid nitrogen; however newer systems are often equipped with silicon drift detectors (SDD) with Peltier cooling systems.
The excess energy of the electron that migrates to an inner shell to fill the newly-created hole can do more than emit an X-ray. Often, instead of X-ray emission, the excess energy is transferred to a third electron from a further outer shell, prompting its ejection. This ejected species is called an Auger electron, and the method for its analysis is known as Auger Electron Spectroscopy (AES). X-ray Photoelectron Spectroscopy (XPS) is another close relative of EDS, utilizing ejected electrons in a manner similar to that of AES. Information on the quantity and kinetic energy of ejected electrons is used to determine the binding energy of these now-liberated electrons, which is element-specific and allows chemical characterization of a sample.

2.3.8. Particle size by Dynamic Light Scattering (DLS) technique

Dynamic light scattering (DLS), sometimes referred to as Quasi-Elastic Light Scattering, is a powerful, well strain-induced broadening arising from crystal imperfections established technique for measuring the size and size distribution of particles in the submicron region, and with the latest technology even lower than 1nm. DLS also measures the dynamic properties and diffusion coefficient of the polymer solution and colloidal suspensions etc. It also provides the information about the polydispersity index of the system under study.

DLS is based on the fact that the particles in the solution undergo Brownian movement induced by their bombardment with the solvent molecules which are themselves moving because of their thermal energy. The motion of the particles is random and they keep on colliding with other suspended particles, while doing so they tend to impart momentum to the suspended particles whose magnitude and direction fluctuate with time. When a laser beam is shined through such a solution, the beam is scattered in all directions with the particles acting as the scattering centers resulting in scattering angle dependent intensity. As the particles experiences the Brownian motion, the scattered intensity pattern also fluctuates at the rate which depends on the size of the particle, as the smaller particles are better scattered as compared to the heavier ones. The statistics of the scattering signals are analyzed with a correlator and the resulting correlation function gives diffusion coefficient, which in turn, yields an overall average, often called the z-average or cumulated average particle diameter/size.

So, the DLS is efficient method in determining the size and shape of the particle and the size profile. Even though the dynamic light scattering is a remarkable
technique for characterization, it is a very sensitive to dust and hence extra care has to be taken during sample preparation.

2.3.9. Photoluminescence spectroscopy

Luminescence emission occurs after an appropriate material has absorbed energy from a source such as ultraviolet or X-ray radiation, electron beams, chemical reactions, and so on. The energy lifts the atoms of the material into an excited state, and then, because excited states are unstable, the material undergoes another transition, back to its unexcited ground state, and the absorbed energy is liberated in the form of either light or heat or both (all discrete energy states, including the ground state, of an atom are defined as quantum states). The excitation involves only the outermost electrons orbiting around the nuclei of the atoms. Luminescence efficiency depends on the degree of transformation of excitation energy into light, and there are relatively few materials that have sufficient luminescence efficiency to be of practical value. Luminescence is emission of light by a substance not resulting from heat; it is thus a form of cold body radiation. It can be caused by chemical reactions, electrical energy, subatomic motions, or stress on a crystal. This distinguishes luminescence from incandescence, which is light emitted by a substance as a result of heating. The term 'luminescence' was introduced in 1888 by Eilhard Wiedemann. Luminescence of inorganic and organic substances results from an emission transition of anions, molecules or a crystal from an excited electronic state to a ground state with lesser energy. Photoluminescence is a special kind of luminescence. Emission wavelength is \( \frac{hc}{(E_1 - E_2)} \), where \( E_1 \) and \( E_2 \) are the initial (higher energy) and final (lower energy) states.

Main processes of luminescence involve
(1) absorption of excitation energy and stimulation of the system into an excited state
(2) transformation and transfer of the excitation energy
(3) emission of light and relaxation of the system into an unexcited condition

Various types of luminescence are:
- Cathodoluminescence: Luminescence due to recombination of EHPs created by energetic electrons. Example: CL mapping system
- Photoluminescence: Luminescence due to recombination of EHPs created by energetic photons. Example: PL mapping system
- Electroluminescence: Luminescence due to recombination of EHPs created by injected electrons and holes. Example: LEDs, Lasers
Chemiluminescence: Luminescence due to light energy obtained from chemical energy. Example: Luminescence in deep sea-water fishes, Mg burning in air.

Two main types of photoluminescence are fluorescence and phosphorescence. Fluorescence is a process where a substance emits light as an effect of the absorption of light of a shorter wavelength. The difference in wavelengths is called Stoke’s Shift. In detail, fluorescence occurs if a substance absorbs light in the form of photons. This leads to a shift of electrons to a higher energy level. But this high energy situation is very unstable, which is why electrons tend to return to their ground state. During this procedure energy is released again in the form of photons that can be seen as a glow. In contrast to phosphorescence, electron energy shift is very fast, in fact in the range of nano seconds (Figure 2.6). Any substance which is able to emit light of a distinct wavelength after excitation with another distinct wavelength is called a fluorochrome. Most fluorescing substances occurring in nature have a broad excitation and emission spectrum, but substances with clearly defined excitation and emission maxima are more useful for fluorescence microscopy.

Similar to fluorescence, phosphorescence is a light-emitting phenomenon where the phosphorescent material is excited with light. Even though it is closely related to fluorescence, it is much slower. In contrast to fluorescence, the re-emission of photons is decelerated by the association of excited electrons energy with a "forbidden" state. Their return to the ground state does not occur as fast as in the case of fluorescence because energy is "trapped". Typical examples of phosphorescent materials are "glow-in-the-dark" toys which can be "charged" with an ordinary light bulb or daylight and then emit light for several minutes or even hours.

![Jablonski diagram showing fluorescence and phosphorescence](image)

**Fig. 2.6** Jablonski diagram showing fluorescence and phosphorescence
All solids including semiconductors have so-called “energy gaps” for the conducting electrons. In order to understand the concept of a gap in energy, first consider that some of the electrons in a solid are not firmly attached to the atoms, as they are for single atoms, but can move from one atom to another. These loosely attached electrons are bound in the solid by differing amounts and thus have different energies. Electrons having energies above a certain value are referred to as conduction electrons, while electrons having energies below a certain value are referred to as valence electrons. This is shown in the diagram where they are labeled as conduction and valence bands. Furthermore, there is an energy gap between the conduction and valence electron states. Under normal conditions electrons are forbidden to have energies between the valence and conduction bands. If a light particle (photon) has energy greater than the band gap energy, then it can be absorbed and thereby raise an electron from the valence band up to the conduction band across the forbidden energy gap (Figure 2.7). In this process of photo excitation, the electron generally has excess energy which it loses before coming to rest at the lowest energy in the conduction band. At this point the electron eventually falls back down to the valence band. As it falls down, the energy it loses is converted back into a luminescent photon which is emitted from the material. Thus, the energy of the emitted photon is a direct measure of the band gap energy, $E_g$. The process of photon excitation followed by photon emission is called photoluminescence.

Fig. 2.7 Phenomenon of photoluminiscence in solids