CHAPTER 2: Experimental

2.1. Materials and reagents: All the solvents, viz. iso-propanol, ethylene glycol, glycerol, methanol and acetone, were of AR grade and these were used as received without further purification. Starting materials, gallium metal (99.99%), Ga(NO$_3$)$_3$.xH$_2$O (99.999%), Zn(OOCCH$_3$)$_2$.2H$_2$O (99.9%), InCl$_3$ (99.999%), SbCl$_3$ (99.9%), Bi(NO$_3$)$_3$.5H$_2$O (99.9%), La(NO$_3$)$_3$.6H$_2$O (99.9%), Ca(NO$_3$)$_2$.H$_2$O (99.9%), SrCl$_2$.6H$_2$O (99.995%), Ba(NO$_3$)$_2$ (99%), Tb(NO$_3$)$_3$.xH$_2$O (99.99%), Tb$_4$O$_7$ (99.99%), Eu(NO$_3$)$_3$.5H$_2$O (99.99%), Eu$_2$O$_3$ (99.99%), Dy$_2$(CO$_3$)$_3$.xH$_2$O (99.9%), Dy(NO$_3$)$_3$.5H$_2$O (99.9%), Ce(NO$_3$)$_3$.6H$_2$O (99.9%), Sm(NO$_3$)$_3$.xH$_2$O (99.9%), Sm$_2$O$_3$ (99.99%), Dy(NO$_3$)$_3$.xH$_2$O (99.9%), and Er(OOCCH$_3$)$_3$.xH$_2$O (99.9%) were obtained from commercial sources. The reagents urea (99.5%), ammonium dihydrogen phosphate (99.9%) and Na$_2$WO$_4$.2H$_2$O (99.5%), were used as obtained for precipitation.

2.2. General synthesis of undoped and lanthanide doped nanomaterials: The nanomaterials were synthesized by co-precipitation method in different organic solvents. A typical synthesis procedure is given below.

Starting materials, chlorides or nitrates, were dissolved in solvents like ethylene glycol, glycerol, water or their mixture. Some solvents like ethylene glycol and glycerol can act both as a solvent as well as a stabilizing agent. These solvents were chosen as they are stable up to a temperature of 180°C and most of the inorganic metal salts (acetates, chlorides, nitrates, etc.) are soluble in them. Further, they are cheaply available, quite stable under ambient conditions and are non-toxic in nature. Precipitating agents depends on the type of the nanomaterial, which is being prepared. For preparing the metal oxide nanoparticles/nanomaterials, urea was used as a precipitating agent. It is superior over other bases like ammonia, NaOH, etc. as it decomposes at above 85°C and generates OH$^-$ ions uniformly throughout the solution leading to homogeneous precipitation. Initially a hydroxide phase
will be formed and subsequently it is converted into oxide by increasing the reaction temperature or by heating the product in a furnace at high temperatures. For the synthesis of phosphate materials, ammonium dihydrogen phosphate was used as a precipitating agent. Ammonium dihydrogen phosphate on heating generates ammonia and phosphate ion, the former creates an alkaline environment, and the latter reacts with metal ions to form the phosphate phase. Alkaline environment facilitate precipitation of metal phosphate. For preparing metal tungstate nanomaterials, sodium tungstate was used as a precipitating agent.

**Procedure:** In a general, soluble metal salt was dissolved in an appropriate solvent and the solution was heated in a silicon oil bath under stirring upto-desired temperature. The precipitating agent was added to the reaction medium at high temperatures depending on the actual material to be synthesized. Temperature of the reaction medium was raised to a value close to reaction temperature so that the nanomaterial/ precursor for nanomaterials start precipitating. The solvent molecules also act as stabilising ligands to prevent aggregation of small particles. The precipitate was separated by centrifugation, washed with ethanol and acetone to remove unreacted species, and dried under ambient conditions. For the synthesis of doped nanoparticles, dopant metal ions were also added to starting chloride or nitrate solution of metal ions. Detailed procedures for the synthesis of individual compound are described below.

2.3 Synthesis of binary oxide nanomaterials:

**Preparation of GaOOH, α-Ga₂O₃ and β-Ga₂O₃ nanorods:** Ga(NO₃)₃.xH₂O, Tb(NO₃)₃.xH₂O, Eu(NO₃)₃.5H₂O and Dy(NO₃)₃.5H₂O were used as starting materials for preparation of undoped GaOOH and lanthanide ions (Eu³⁺, Tb³⁺ and Dy³⁺) doped GaOOH nanorods. In a typical procedure for making GaOOH sample, Ga(NO₃)₃.xH₂O (1.0 g) was dissolved in 20 ml water in a 100 ml round bottom flask. The solution was slowly heated upto 70°C in a silicon oil bath while stirring followed by addition of urea (5.0 g). Temperature was
raised to 100°C and refluxed until a slightly turbid solution was obtained. At this temperature, sufficiently high concentration of OH⁻ is generated in the medium leading to high concentration of GaOOH nuclei, which facilitates growth of the nuclei into nanorod morphology. The temperature was maintained at this value for 2 hours. After the reaction, the precipitate was collected by centrifugation and was then washed two times with ethyl alcohol and three times with acetone followed by drying under ambient conditions. For Eu³⁺, Tb³⁺ and Dy³⁺ doped samples same procedure was used except that, Eu(NO₃)₃.5H₂O, Tb(NO₃)₃.xH₂O and Dy(NO₃)₃.5H₂O were used respectively along with Ga(NO₃)₃.xH₂O (1.0 g) and urea (5.0 g) as the starting materials. As prepared samples were heated in a furnace at 500 and 900°C for 10 hours to convert GaOOH and GaOOH:Ln³⁺ to α and β forms of Ga₂O₃ and Ga₂O₃:Ln³⁺.

**Preparation of Sb₂O₃ nanorods with and without Eu³⁺ ions:** For the synthesis of nanorods without Eu³⁺, SbCl₃ (0.5 g) was dissolved in conc. HCl and evaporated repeatedly by adding water drop wise while stirring. Repeated evaporation was done to remove excess HCl and drop wise addition of water was necessary for preventing the rapid hydrolysis of SbCl₃ leading to the formation of Sb(OH)₃ precipitate. Around 2 ml solution of SbCl₃ left over after the repeated evaporation was mixed with 20 ml of iso-propanol followed by the addition of 20% ammonium hydroxide solution drop wise while stirring until precipitation. This precipitate was centrifuged and washed several times with ethanol and acetone to remove free solvent and unreacted species. For samples containing different amounts of Eu³⁺ ions (2, 5 and 10 atom % Eu³⁺ with respect to Sb³⁺), same procedure was used except that Eu₂O₃ was dissolved in concentrated HCl and added to the acidic solution of SbCl₃ prior to the reaction. Bulk Sb₂O₃ sample with Eu³⁺ (5 atom % with respect to Sb³⁺) ions was obtained by hydrolysis of SbCl₃ and EuCl₃ in water at room temperature. For the purpose of comparison,
Eu\(^{3+}\) ions were also subjected to same reaction conditions as that used for the preparation of Sb\(_2\)O\(_3\) nanorods and the resulting precipitate was, centrifuged, washed and dried.

2.4 Synthesis of phosphate nanomaterials:

**Preparation of undoped GaPO\(_4\) and Eu\(^{3+}\) ions containing GaPO\(_4\) nanoparticles:** For preparation of GaPO\(_4\) and Eu\(^{3+}\) ions containing GaPO\(_4\) nanoparticles, Ga metal and Eu\(_2\)O\(_3\) were used as starting materials. For the synthesis of 5 at % Eu\(^{3+}\) (95 at % Ga\(^{3+}\) and 5 at % Eu\(^{3+}\)) containing GaPO\(_4\) nanoparticles, gallium metal (0.21 g) and Eu\(_2\)O\(_3\) (0.0265 g) (5 atom % Eu\(^{3+}\) with respect to Ga\(^{3+}\)) were dissolved in concentrated HCl in a beaker by heating and the excess acid was evaporated out repeatedly. To this solution, glycerol (20 ml) was added and transferred into a two-necked RB flask. The solution was slowly heated up to 70°C followed by addition of ammonium dihydrogen phosphate (0.35 g). Temperature was then raised to 130°C and maintained at this value for 2 hours. After the reaction, the precipitate was collected by centrifugation and then washed three times with ethyl alcohol and two times with acetone followed by drying under ambient conditions. A similar procedure was followed for the synthesis of undoped, 2.5 and 10 at % Eu\(^{3+}\) containing GaPO\(_4\) nanoparticles.

**Preparation of undoped and lanthanide doped SbPO\(_4\) nanomaterials:** For preparation of SbPO\(_4\) and lanthanide ions (Tb\(^{3+}\) and Ce\(^{3+}\)-Tb\(^{3+}\)) doped SbPO\(_4\) nanomaterials, SbCl\(_3\), Tb\(_4\)O\(_7\), Eu\(_2\)O\(_3\), Ce(NO\(_3\))\(_3\)\(\cdot\)6H\(_2\)O were used as starting materials. In a typical procedure for making SbPO\(_4\):Tb\(^{3+}\)(5%) sample (SbPO\(_4\) sample doped with 5 at % Tb\(^{3+}\) ions), SbCl\(_3\) (0.5 g) and Tb\(_4\)O\(_7\) (0.01 g) (5 at %) were dissolved in concentrated HCl in a beaker and the excess acid was repeatedly evaporated. To this solution, ethylene glycol (12 ml) and glycerol (8 ml) were added and it was transferred into a two-necked 100 ml round bottom flask. The solution was slowly heated up to 70°C followed by addition of ammonium dihydrogen phosphate (0.75g). Temperature was raised to 90°C and maintained till slightly turbid solution was obtained. Finally, temperature was raised to 120°C and maintained at this value for 2 hours. After the
reaction, the precipitate was collected by centrifugation and then washed two times with acetone and three times with ethyl alcohol followed by drying under ambient conditions. Samples obtained by above method were dispersible in water and methanol. Same procedure was also employed for making SbPO$_4$ samples containing 1 and 2.5 at % Tb$^{3+}$ ions (denoted as SbPO$_4$·Tb$^{3+}$ (1%) and SbPO$_4$·Tb$^{3+}$ (2.5%)). For preparing Tb$^{3+}$, Ce$^{3+}$ co-doped samples same procedure was used except that, 0.01 g of Tb$_4$O$_7$ (5 at %) and 0.012 g (2.5 at %) of Ce(NO$_3$)$_3$·6H$_2$O were used respectively along with 0.5 g of SbCl$_3$ (sample is denoted as SbPO$_4$:Ce$^{3+}$(2.5 at %), Tb$^{3+}$(5 at %)).

**Preparation of SbPO$_4$:Ce$^{3+}$(2.5 at %), Tb$^{3+}$(5 at %) nanomaterials dispersed in silica:**

For the preparation of SbPO$_4$: Ce$^{3+}$ (2.5 at %), Tb$^{3+}$(5 at %) nanomaterials dispersed in silica (represented as SbPO$_4$: Ce$^{3+}$(2.5 at %), Tb$^{3+}$(5 at %)-SiO$_2$), SbCl$_3$ (0.5 g), Tb$_4$O$_7$ (0.01 g) and Ce(NO$_3$)$_3$·6H$_2$O (0.012 g) were dissolved in con. HCl and excess acid was evaporated by adding distilled water drop wise. To this solution, ethylene glycol (12 ml) and glycerol (8 ml) were added and it was transferred into a two-necked 100 ml RB flask. The solution was slowly heated upto 70°C while stirring followed by addition of ammonium dihydrogen phosphate (0.75 g). Temperature was raised to 120°C resulting in the formation of a turbid solution. After 10 min, 0.7 ml of tetraethyl orthosilicate (TEOS) was added to this. It was then refluxed for 2 hours at 120°C. The precipitate was centrifuged, washed with ethanol and acetone.

**Synthesis of undoped and lanthanide doped BiPO$_4$ nanomaterials:** For preparation of undoped BiPO$_4$ and lanthanide ions (Tb$^{3+}$, Eu$^{3+}$, Dy$^{3+}$, Sm$^{3+}$) doped BiPO$_4$ nanomaterials, Bi(NO$_3$)$_3$·5H$_2$O, Tb$_4$O$_7$, Eu$_2$O$_3$, Dy$_2$(CO$_3$)$_3$·xH$_2$O, Sm$_2$O$_3$ were used as starting materials. For the synthesis of Eu$^{3+}$ doped BiPO$_4$, Bi(NO$_3$)$_3$·5H$_2$O (1.0 g) and Eu$_2$O$_3$ (0.011 g)(2.5 at %) were dissolved in concentrated HCl in a beaker and the excess acid was evaporated out repeatedly by adding water. To this solution, 20 ml of ethylene glycol was added and it was
transferred into a two-necked RB flask. An aqueous solution (3 ml) of ammonium dihydrogen phosphate (0.3 g) was added with stirring. The solution was heated at different temperatures viz. 75, 100, 125 and 185°C for two hours. The precipitate obtained was washed with methanol and acetone to remove unreacted species and dried under ambient conditions. The same procedure was followed for the synthesis of other lanthanide ions doped samples.

2.5 Synthesis of gallate nanomaterials:

**Synthesis of undoped, In\(^{3+}\) and Ln\(^{3+}\) doped ZnGa\(_2\)O\(_4\) nanoparticles:** For the preparation of ZnGa\(_2\)O\(_4\) nanoparticles gallium metal and Zinc acetate were used as starting materials. Gallium metal (0.2 g) was dissolved in concentrated HCl containing few drops of HNO\(_3\) in a beaker and the excess acid was removed by repeated evaporation by adding water. This solution was transferred into a two-necked RB flask, containing appropriate amount of zinc acetate. Ethylene glycol (25 ml) and distilled water (10 ml) were added to this mixture. The solution was slowly heated up to 100°C followed by the addition of urea (3.0 g). It was heated at 120°C whereupon turbidity appeared. Temperature of the reaction was maintained for 2 hours to complete the reaction. The precipitate was collected by centrifugation and then washed three times with ethyl alcohol and two times with acetone followed by drying under ambient conditions. This process was repeated for different ratios of solvent to precursor concentration as well as ethylene glycol to water. For In\(^{3+}\), Eu\(^{3+}\) and Tb\(^{3+}\) doped samples same procedure was followed except addition of appropriate amounts of InCl\(_3\), Eu\(_2\)O\(_3\) and Tb\(_4\)O\(_7\) was carried out while dissolving gallium metal in concentrated HCl.

**Preparation of In\(^{3+}\) doped ZnGa\(_2\)O\(_4\) nanoparticles incorporated PMMA matrix:** For incorporating nanoparticles in polymer, the procedure reported by Gonsalves, et al. [115] was employed. The method is described below. Around 50 mg of ZnGa\(_2\)O\(_4\) nanoparticles was dispersed in one ml of methyl methacrylate (MMA) by sonicating for one hour under argon atmosphere. Around 5 mg of azobisisobutyronitrile (AIBN) was added to this mixture and
heated for 2 hrs at 70°C under argon atmosphere. White solid was obtained and this solid was dissolved in CHCl₃ and re-precipitated with methanol. The precipitate was separated by centrifugation and dried under ambient conditions. For preparing thin polymer films containing the nanoparticles, the white solid obtained was dissolved in CHCl₃ and spin coated on a quartz substrate at a spinning rate of 2500 rpm.

2.6. Synthesis of un-doped and lanthanide doped MWO₄ (M = Ca, Sr, Ba) nanomaterials: Starting materials used for the synthesis of undoped and lanthanide doped metal tungstates were Ca(NO₃)₂.H₂O, SrCl₂.6H₂O, Ba(NO₃)₂, Eu(NO₃)₃.5H₂O, Tb(NO₃)₃.xH₂O, Dy(NO₃)₃.xH₂O, Sm(NO₃)₃.xH₂O and Er(OOCCH₃)₃.xH₂O. For the synthesis of undoped metal tungstates, 2.12 mmol of metal salt was dissolved in 20 ml of ethylene glycol while stirring. Around 2.12 mmol of Na₂WO₄.2H₂O was added to this solution and stirring was continued for two hours. The precipitate formed was separated by centrifugation and washed with methanol and acetone to remove unreacted species. For the synthesis of lanthanide doped metal tungstates, same procedure was followed except that the addition of 2 atom % lanthanide salts to metal salt solution was done prior to the addition of Na₂WO₄.2H₂O.

2.7. Characterization Techniques: During the present investigation, various characterization techniques were employed and they are briefly discussed below.

2.7.1. X-Ray Diffraction: X-rays are invisible, electrically neutral, electromagnetic radiations. Their frequencies are intermediate between the ultra-violet (UV) and gamma radiations with wavelength (λ) ranging from approximately 0.04 Å to 1000 Å. When the X-rays are incident on a solid material (grating), they are either elastically/in-elastically scattered or absorbed. The elastic scattering of X-rays is known as Bragg scattering and follows the Bragg equation (equation 7)

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

………………………… (7)
Where $\lambda$ is the wavelength of X-rays, $\theta$ is glancing angle, $d$ is interplanar distance and $n$ is order of diffraction. Depending on the interplanar distance and angle of diffraction, the diffracted/scattered beam will interfere with each other giving bright (constructive interference) and dark (destructive interference) fringes.

**Powder X-ray diffraction**: X-ray diffraction experimental setup requires an X-ray source, sample under investigation and a detector to pick up the diffracted X-rays. A block sketch of the typical powder diffractometer is shown in the Fig. 11. The X-ray beam passes through the soller and divergence slits and then fall on the sample which is spread uniformly over a rectangular area of a glass slide. The X-rays scattered (diffracted) from the sample pass through the soller and receiving slits and then fall on a monochromator before detection. The monochromator separates out the stray wavelength radiation as well as any fluorescent radiation emitted by the sample. The details of the X-ray production and the typical X-ray spectra are explained in several monographs [116, 117].

![Fig.11 X-Ray diagram of a typical reflection mode diffractometer.](image)

**Data collection and Analysis**: The output of the diffraction measurement is obtained as plot of intensity of diffracted X-rays versus Bragg angle. The data collection protocols often depend on the specific purpose for which the diffraction experiment is being carried out. In general a short time scan in the 2$\theta$ range of 10 to 70° is sufficient for the identification of phase of a well crystalline inorganic material. The scan time can be optimized for getting
good intensity peaks. In the present study, the observed diffraction patterns were compared
with JCPDS (Joint Committee on Powder Diffraction Standards, 1974) files available for
reported crystalline samples. The unit cell parameters were refined by a least squares method
using the computer software “Powderx”. The average crystallite size of the nano powders
was estimated from the full width at half maximum (FWHM) of the intense peak in the XRD
pattern using the Scherrer’s formula, which is given by equation 8

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  \hspace{1cm} (8)

Where D is the thickness of the crystal (in angstroms), \( \lambda \) the X-ray wavelength and \( \theta \) the
Bragg angle. The line broadening, \( \beta \), is measured from the extra peak width at half the peak
height and is obtained from the Warren formula (equation 9):

\[ \beta^2 = \beta_M^2 - \beta_S^2 \]  \hspace{1cm} (9)

Where \( \beta_M \) is the measured peak width in radians at half maxima and \( \beta_S \) is the measured peak
width in radians at half maxima of the peak corresponding to standard material (silicon).

In the present study, Philips 1710 diffractometer based on the Bragg-Brentano
reflection geometry, was used for the characterization of all the samples. The Cu-K\( \alpha \) from
sealed tube was used as the incident beam. A Ni foil was used as a filter and the diffracted
beam was monochromatised with a curved graphite single crystal. The Philips (PW-1710)
diffractometer is attached with a proportional counter (Argon filled) for the detection of X-
rays. The X-ray tube rating was maintained at 30 kV and 20mA. The goniometer was
calibrated for correct zero position using silicon standard. Samples are well grounded and
made in the form of a slide. As all the micro crystals are randomly oriented, at any point on
the sample different planes from crystals will be exposed to X-rays.

2.7.2. Electron Microscopy: Micro-structural characterization has become important for all
types of materials as it gives substantial information about the structure-property correlation.
Micro-structural characterization broadly means ascertaining the morphology, identification of crystallographic defects and composition of phases, estimating the particle size, etc. Electron microscopic techniques are extensively used for this purpose. Electron microscopy is based on the interaction between electrons (matter wave) and the sample. In the present study, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) have been used to characterize the nano powders. The principle and experimental details of these two techniques are given below.

**Scanning Electron Microscopy (SEM):** In a typical scanning electron microscope, a well-focused electron beam is incident and scanned over the sample surface by two pairs of electro-magnetic deflection coils. The signals generated from the surface by secondary electrons are detected and fed to a synchronously scanned cathode ray tube (CRT) as intensity modulating signals [118, 119]. Thus, the specimen image is displayed on the CRT screen. Changes in the brightness represent changes of a particular property within the scanned area of the specimen. Schematic representation of SEM is shown in Fig.12.

![Schematic representation of SEM microscope.](image-url)
For carrying out SEM analysis, the sample must be vacuum compatible (~ $10^{-6}$ Torr or more) and electrically conducting. The surfaces of non-conductive materials are made conductive by coating with a thin film of gold or platinum or carbon. In this study, the SEM technique was used to study the microstructure evolution of nanocrystalline powders and EDS (energy dispersive X-ray spectroscopy) is used for the compositional analysis.

In the present study, SEM instrument used was from Seron Inc. (Model AIS 2100) having standard tungsten filament. An accelerating voltage of 20 kV and magnification of 10kx was used for recording the micrographs. The samples were made in the form of slurry with isopropyl alcohol and spread over mirror polished single crystal of Si substrate prior to its mounting on the stub.

**Transmission Electron Microscopy (TEM):** In TEM, a beam of focused high-energy electrons is transmitted through the sample to form an image, which reveals information about its morphology, crystallography and particle size distribution at a spatial resolution of ~1 nm. TEM is unique as it can focus on a single nanoparticle and can determine its crystallite size. This technique is applicable to a variety of materials such as metals, ceramics, semiconductors, minerals, polymers, etc. [120, 121]. TEM setup consists of an electron gun, voltage generator, vacuum system, electromagnetic lenses and recording devices and the schematic diagram of TEM is shown in Fig.13 (a). Usually thermionic gun (tungsten filament, LaB$_6$ crystal, etc.) or field emission gun is used as an electron source to illuminate the sample. The electrons thus produced are accelerated at chosen voltages by a voltage generator. The electron beam after passing through the condenser lens system is directed towards a thin sample. Typically TEM specimen thickness is in the range of 50 to 100 nm and should be transparent to the electron beam. The microscope column is maintained at high vacuum levels to prevent scattering of electrons by the atmosphere inside the microscope. Information is obtained from both transmitted electrons (i.e. image mode) and diffracted
electrons (i.e. diffraction mode). In TEM, contrast formation depends greatly on the mode of operation. In conventional TEM, contrast is obtained by two modes namely the mass-thickness contrast and the diffraction contrast and both are based on amplitude contrast. In high resolution transmission electron microscopy (HRTEM), image contrast is due to phase contrast. Mechanism of all these types of contrasts is briefly discussed below.

**Mass-thickness contrast**: This is the common mode of operation in TEM and it is called as bright field imaging. In this mode, the contrast formation is obtained directly by occlusion and absorption of electrons in the sample. Thicker regions of the sample or regions with a higher atomic number will appear dark, while the regions with no sample in the beam path will appear bright – hence the term "bright field". The image is in effect assumed to be a simple two-dimensional projection of the sample. The effect of thickness and mass number of the sample on the brightness of the image can be seen in the Fig.13 (b).

![Transmission Electron Microscope](a)

![Mass-thickness contrast](b)

Fig.13. (a) Simplified ray diagram of TEM, (b) Mass-thickness contrast.
**Diffraction contrast:** This mode of operation is also known as dark field imaging. In the case of a crystalline sample, the electron beam undergoes Bragg scattering and it disperses electrons into discrete locations. By the placement of apertures in these locations, i.e. the objective aperture, the desired Bragg reflections can be selected (or excluded), thus only parts of the sample that are causing the electrons to scatter to the selected reflections will end up projected onto the imaging apparatus. A region without a specimen will appear dark if there are no reflections from that region. This is known as a dark-field image. This method can be used to identify lattice defects in crystals. By carefully selecting the orientation of the sample, it is possible not only to determine the position of defects but also to determine the type of defect present.

**Phase contrast:** Among all the techniques used to obtain structural information of materials, high resolution electron microscopy (HREM) has the great advantage that it yields information about the bulk structure, projected along the direction of electron incidence at a resolution comparable to the inter atomic distances. This enables the study of complicated structures, crystal defects, precipitates and so forth, down to the atomic level. In HRTEM, phase contrast is used for the imaging. High resolution images are formed by the interference of elastically scattered electrons, leading to a distribution of intensities that depends on the orientation of the lattice planes in the crystal relative to the electron beam. Therefore, at certain angles the electron beam is diffracted strongly from the axis of the incoming beam, whilst at other angles the beam is completely transmitted. In the case of high-resolution imaging, this allows the arrangement of atoms within the crystal lattice to be deduced. For HREM measurements, sample should be very thin.

**Selected area electron diffraction (SAED):** An aperture in the image plane is used to select the diffracted region of the specimen, giving site-selective diffraction analysis. SAED patterns are a projection of the reciprocal lattice, with lattice reflections showing as sharp
diffraction spots. By tilting a crystalline sample to low-index zone axes, SAED patterns can be used to identify crystal structures and measure lattice parameters. Figure 14 shows electron diffraction in (a) single crystal, (b) polycrystalline and (c) nanocrystalline materials. Electron diffraction pattern of polycrystalline or nanocrystalline materials can be indexed by using equation 10

\[ R d = \lambda L \]  

(10)

Where \( R \) is the radius of diffraction ring, \( L \) is camera length, \( \lambda \) is the electron wavelength, and \( d \) is the spacing corresponding to planes.

Fig.14. Electron diffraction patterns from (a) single crystal, (b) polycrystalline materials and (c) nanocrystalline materials [120].

In the present study, Transmission electron microscopic (TEM) measurements (bright field low magnification and lattice imaging) were performed using 200 keV electrons in JEOL 2010 UHR TEM microscope. Samples were dispersed in methanol and a drop of this solution was added on a carbon coated copper grid. These samples were dried properly prior to load in TEM.

2.7.3. Atomic Force Microscope (AFM): AFM measures the topography of conductors, semiconductors, and insulators with a force probe located within a few Å of the sample surface [122]. AFM images are recorded by moving fine tip attached to a cantilever across
the surface of the sample while the tip movements normal to the surface are measured. The deflections occurred in the tip, due to the interaction forces between the tip and sample surface, can be measured by focusing a laser beam onto cantilever and detecting the reflected light from the cantilever using a position sensitive detector. Schematic diagram of atomic force imaging is shown in Fig 15 (a). As the tip is rastered over the surface, a feedback mechanism is employed to ensure that the piezo-electric motors maintain a constant tip force or height above the sample surface. The tip movements normal to the surface are digitally recorded and can be processed and displayed in three-dimensions by a computer. This technique has a lateral resolution of 1 to 5 nm. AFM is typically used to obtain a three-dimensional surface image or to determine the surface roughness of thin films and crystal grains. There are mainly two types of AFM modes, namely the contact mode and the semi contact/taping mode, which are used for imaging the samples. The schematic representation of the different types forces acting between tip and sample in the two methods of imaging is shown in Fig.15 (b) and are described below.

![Diagram of AFM imaging](image)

**Fig.15.** (a) Principle of AFM imaging, (b) variation of interaction force versus distance between the AFM tip and substrate.

(1) Contact mode: Here, the force between the probe tip and substrate is repulsive, and it is within the range of $10^{-8}$ to $10^{-7}$ N. The force is set by pushing a cantilever against the sample
surface. The contact mode can obtain a higher atomic resolution than the other modes, but it may damage a soft material due to excessive tracking forces applied from the probe on the sample. Unlike the other modes, frictional and adhesive forces will affect the image.

(2) Non-contact/tapping mode: Here, the main interaction force between the probe tip and the substrate is attractive due to van der Waals force and it is in the range of $10^{-10}$ to $10^{-12}$ N. In this mode, cantilever oscillates in the attractive region and its oscillation frequency gets modulated depending on the sample surface features. The tip is 5 to 150 nm above the sample surface. The resolution in this mode is limited by the interactions with the surrounding environment.

In the present study, Atomic force microscopic (AFM) measurements were performed in contact mode using an AFM instrument from Ms. NT-MDT (solver model) with a 50 µm scanner head. Samples were dispersed in methanol and a drop of this solution was added on highly oriented pyrolytic graphite (HOPG)/ mica sheets. These samples are dried properly before loading in AFM.

2.7.4. **Vibrational spectroscopy:** Vibrational spectroscopic techniques are extensively used to identify the nature of different linkages present in a material. These methods also give valuable information regarding the symmetry of different vibrational units. Two types of vibrational techniques, namely IR and Raman spectroscopy are used in the present study and the principle is briefly described below.

**IR spectroscopy:** Vibrations of bonds and groups which involve a change in the dipole moment results in the absorption of infrared radiation which forms the basis of IR spectroscopy. Modern IR instruments are based on Fourier transformation method to improve the signal to noise ratio. Unlike conventional IR instrument, in FTIR instrument, all the frequencies are used simultaneously to excite all the vibrational modes of different types of bonds/linkages present in the sample. This reduces the experimental time considerably.
In the present study, all infrared experiments were carried out using a Bomem MB102 FTIR machine having a range of 200-4000 cm\(^{-1}\) and with resolution of 4 cm\(^{-1}\). IR radiation was generated from globar source (silicon carbide rod). The instrument used CsI single crystal, as the beam splitter and deuterated triglycine sulphate (DTGS) as a detector. Prior to IR measurements, the samples were ground thoroughly by mixing with dry KBr powder, made in the form of a thin pellet and introduced into the sample chamber of the instrument.

**Raman spectroscopy:** Raman spectroscopy is a very convenient technique for identification of crystalline or molecular phases, for obtaining structural information. Backscattering geometries allow films, coatings and surfaces to be easily analyzed. Ambient atmosphere can be used and no special sample preparation is needed for analyzing samples by this technique. The principle is briefly described below. When an intense beam of monochromatic light is passed through a substance, a small fraction of light is scattered by the molecules in the system. The electron cloud in a molecule can be polarized (deformed) by the electric field of the incident radiation. If we apply an oscillating electric field (the electric field vector of the light wave) to the molecule, the deformation of the electron cloud will also oscillate with the same frequency (Vo) of the incident light beam. This oscillation of the electron cloud produces an oscillating dipole that radiates at the same frequency as the incident light. This process is called Rayleigh scattering. The Rayleigh-scattered radiation is emitted in all directions. Since only about 0.1% of the light is scattered, we must use as intense a source as possible and a laser fulfills this requirement admirably. There is a small but finite probability that the incident radiation will transfer part of its energy to one of the vibrational or rotational modes of the molecule. As a result, the scattered radiation will have a frequency \(Vo - Vm\), where \(Vm\) is the absorbed frequency. Similarly, there is a slight chance that molecules in excited vibrational or rotational states will give up energy to the light beam. In this case the scattered radiation will have a higher frequency \(Vo + Vm\). Thus, it is possible to observe
three types lines in the scattered radiation: One line at Vo corresponding to the Rayleigh scattering and two Raman lines, one at Vo + Vm known as the anti-Stokes line, and the other at Vo - Vm, known as the Stokes line. Since there are fewer molecules in the upper vibrational state than in the lower vibrational state, the intensity of the anti-Stokes line is much less than that of the Stokes line. The two Raman lines are extremely weak compared to the intensity of the Rayleigh scattered light and is less than $10^{-7}$ of the intensity of the incident light [123].

In the present study, Raman spectra were recorded on a home-made Raman spectrometer using 488 nm line from an air cooled Argon ion laser. The spectra were collected using a grating with 1200 groves/mm with a slit width of ~50 micron (yielding a resolution of ~ 1 cm$^{-1}$), along with Peltier cooled CCD and a Razor edge filter.

2.7.5. Nuclear magnetic resonance (NMR) Spectroscopy: Nuclear magnetic resonance spectroscopy is a technique that exploits the nuclear magnetic properties of atomic nuclei and can give valuable information about the structure, dynamics and chemical environment of around a particular nucleus in a molecule/lattice.

Chemical shift: The chemical shift of any nucleus is defined as the difference between its resonance frequency and the resonance frequency of the same nuclei in a reference sample and can be expressed by the equation 11

$$
\delta = \frac{\omega - \omega_0}{\omega_0} \times 10^6 \quad \text{.......................... (11)}
$$

where $\omega$, $\omega_0$ represent resonance frequencies of nuclei in the sample and in the reference, respectively.

Chemical shielding interaction: Chemical shift arises because of the effective magnetic field felt by nuclei is brought about by the polarization effect of electron cloud around the nuclei created by the applied magnetic field. Since this is particularly sensitive to the
configuration of valance electrons, which is governed by the nature of chemical bonding, this aspect has been labeled as chemical shielding interaction. The Hamiltonian for this interaction can be given by the equation 12 \[124, 125\].

\[ H_{\sigma} = \gamma I_z \sigma B_0 \] (12)

where \( \sigma \) is a second rank (3x3) tensor known as chemical shielding tensor. This tensor can be diagonalised for a specific principal axis system and \( \sigma_{11}, \sigma_{22}, \sigma_{33} \) are the corresponding diagonal components. The isotropic component of the chemical shift tensor can be expressed by the relation (equation 13):

\[ \sigma_{iso} = \frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33}) \] (13)

The symmetry parameter is defined by equation 14:

\[ \eta = \frac{\sigma_{22} - \sigma_{11}}{\sigma_{33} - \sigma_{iso}} \] (14)

Due to the presence of chemical shielding anisotropy, the nuclear precessional frequency depends on the orientation of principal axis system with respect to the external applied magnetic field and can be expressed by the relation (equation 15) \[125\]

\[ \omega_p(\theta, \phi) = \gamma B_0 \left\{ \left(1 - \sigma_{11}\right)^2 \cos^2 \phi \sin^2 \theta + \left(1 - \sigma_{22}\right)^2 \sin^2 \phi \sin^2 \theta + \left(1 - \sigma_{33}\right)^2 \cos^2 \theta \right\}^{1/2} \] (15)

where \( \theta \) and \( \Phi \) represent the orientation of principal axis system with applied magnetic field direction. For axial symmetry \( \eta = 0 \) and the precession frequency can be expressed by the relation (equation 16)

\[ \omega_p(\theta) = \gamma B_0 \left[ 1 - \sigma_{iso} - \Delta \sigma \left(3 \cos^2 \theta - 1\right)/3 \right] \] (16)

For values of \( \theta = 54.7^\circ \) the term \( 3 \cos^2 \theta - 1 \) becomes zero and the dependence of chemical shielding anisotropy term on Larmor frequency gets averaged out to a very small value.

In solution NMR spectroscopy, the molecular motion averages out dipolar interactions and anisotropic effects. This is not so in the solid state and the NMR spectra of...
solids tend to be broadened because of (a) magnetic interactions of nuclei with the surrounding electron cloud (chemical shielding interaction), (b) magnetic dipole – dipole interactions among nuclei and (c) interactions between electric quadrupole moment and surrounding electric field gradient. Hence, it is difficult to get any meaningful information from such patterns. However, by using suitable experimental strategies, such interactions can be averaged out, thereby improving the information obtained from solid-state NMR patterns. One such technique used to get high-resolution solid-state NMR pattern in solids is the magic angle spinning nuclear magnetic resonance (MAS NMR) technique. In the following section brief account of the MAS NMR technique has been given.

**Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR):** MAS NMR technique involves rotating the powder samples at high speeds, at an angle of 54.7° (magic angle) with respect to the applied magnetic field direction. When \( \theta = 54.7° \), the term \( 3\cos^2\theta - 1 \) becomes unity. Since Hamiltonian for different anisotropic interactions have \( 3\cos^2\theta - 1 \) term, these anisotropic interactions get averaged out in time during fast spinning. This is schematically shown in Fig.16 and explained below.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig16.png}
\caption{Principle of MAS NMR experiment}
\end{figure}

At sufficiently fast spinning speeds, the NMR interaction tensor orientations with initial angles of \( \theta_1 \) and \( \theta_2 \) relative to \( B_0 \) have orientaional averages of 54.7°, resulting in the conversion of \( 3\cos^2\theta - 1 \) term in expressions corresponding to various interactions to a very
small value, thereby giving rise to sharp NMR peaks. Thus, the MAS NMR technique simplifies the solid-state NMR patterns and individual chemical environments can be correlated with corresponding chemical shift values obtained from these samples [125, 126].

Although, MAS is an efficient technique employed for getting high resolution NMR patterns from solid samples, in many cases, due to spinning, side bands, which are mirror images of the isotropic peak and spread from the isotropic peak by integer multiples of the spinning frequency, appear along with the central isotropic peak for nuclei having wide range of chemical shift values. For nuclei having a nuclear spin value $\frac{1}{2}$, sideband pattern is a measure of the chemical shift anisotropy and valuable information regarding the symmetry of the electronic environment around a probe nuclei can be obtained from the intensity distribution of sidebands. However, in the presence of large number of isotropic peaks, the number of sidebands also increases, and there can be overlap between the sidebands and isotropic peaks, which makes the MAS NMR pattern complicated.

In the present study, $^{31}$P MAS NMR patterns were recorded using a 500 MHz Bruker Avance machine with a $^{31}$P basic frequency of 202.4 MHz. The samples were packed inside 2.5 mm rotors and subjected to various spinning speeds ranging between 5000 to 10000 Hz. The chemical shift values are expressed with respect to 85% H$_3$PO$_4$ solution. The typical 90° pulse duration and relaxation delay are 4 $\mu$s and 5s, respectively.

2.7.6. Photoluminescence spectroscopy: Photoluminescence (PL) is a process, in which a substance absorbs photons (electromagnetic radiation) and then re-radiates photons. Quantum mechanically, this can be described as an excitation to a higher energy state by absorption of photon and then a return to a lower energy state accompanied by the emission of a photon.

The schematic representation of spectrofluorimeter can be seen in Fig.17. The light from an excitation source passes through a monochromator, and strikes the sample. A proportion of the incident light is absorbed by the sample, and some of the molecules in the
sample fluoresce. The fluorescent light is emitted in all directions. Some of this fluorescent light passes through a second monochromator and reaches a detector, which is usually placed at 90° to the incident light beam to minimize the risk of transmitted or reflected incident light reaching the detector. Various light sources may be used as excitation sources, including lasers, photodiodes and lamps (xenon arcs and mercury-vapor lamps).

Xenon arc lamp has a continuous emission spectrum with nearly constant intensity in the range from 300-800 nm and a sufficient irradiance for measurements down to 200 nm. A monochromator transmits light of an adjustable wavelength with an adjustable tolerance. The most common type of monochromator utilizes a diffraction grating wherein a collimated light illuminates a grating and exits with a different angle depending on the wavelength. The monochromator can then be adjusted to select which wavelengths to transmit. The most commonly used detector is photomultiplier tube (PMT).

**Excitation and Emission spectra:** The spectrofluorometer with dual monochromators and a continuous excitation light source can record both excitation spectrum and emission
spectrum. When measuring emission spectra, the wavelength of the excitation light is kept constant, preferably at a wavelength of high absorption, and the emission monochromator scans the spectrum. For measuring excitation spectra, the wavelength passing through the emission monochromator is kept constant and the excitation monochromator is subjected to scanning. The excitation spectrum generally is identical to the absorption spectrum as the emission intensity is proportional to the absorption. Lifetime and quantum yields are two important properties of a phosphor and they can tell us about the quality of a phosphor.

**Lifetime**: The lifetime of the excited state is defined by the average time the molecule spends in the excited state prior to return to the ground state and is expressed by the equation 17 [127].

\[
\tau = \frac{1}{k_r + k_{nr}} \quad \text{..................... (17)}
\]

Where \( k_r \) is the radiative decay rate, \( k_{nr} \) is the non-radiative decay rate. The radiative lifetime \( \tau_0 \) is defined as the inverse of the radiative emission rate i.e, \( \tau_0 = k_r^{-1} \). Lifetime measurements were performed using both time correlated single photon counting (TCSPC) and multi channel scaling (MCS) modes.

**Quantum yield**: It is defined as the ratio of the emitted to the absorbed photons. The quantum efficiency \( \eta \) can also expressed in terms of the radiative lifetime (\( \tau_0 \)) and luminescence lifetimes (\( \tau \)) by the equation 18 [127].

\[
\eta = \frac{k_r}{k_r + k_{nr}} = \frac{\tau}{\tau_0} \quad \text{......................... (18)}
\]

In the present study all luminescence measurements were carried out by using an Edinburgh Instruments’ FLSP 920 system, having a 450W Xe lamp, 60 W microsecond flash lamp and hydrogen filled nanosecond flash lamp (operated with 6.8 kV voltage and 40 kHz.
pulse frequency) as excitation sources for steady state and for lifetime measurements. Red sensitive PMT was used as the detector. Quantum yield was measured by using integrating sphere which is coated inside with BaSO$_4$ as a reflector.

2.7.7. Thermal analysis: Thermal analysis methods are essential for understanding the compositional and heat changes involved during reaction. They are useful for investigating phase changes, decomposition, and loss of water or oxygen and for constructing phase diagrams.

Thermo gravimetric analysis (TGA): In TGA, the weight of a sample is monitored as a function of time as the temperature is increased at a controlled uniform rate. Loss of water of crystallization or volatiles (such as oxygen, CO$_2$, etc.) is revealed by a weight loss. Oxidation or adsorption of gas shows up as a weight gain.

Differential thermal analysis (DTA): A phase change is generally associated with either absorption or evolution of heat. In DTA experiments, the sample is placed in one cup, and a standard sample (like Al$_2$O$_3$) in the other cup. Both cups are heated at a controlled uniform rate in a furnace, and the difference in temperature ($\Delta T$) between the two is monitored and recorded against time or temperature. Any reaction involving heat change in the sample will be represented as a peak in the plot of $\Delta T$ vs T. Exothermic reactions give an increase in temperature, and endothermic reaction leads to a decrease in temperature and the corresponding peaks appear in opposite directions.

In the present study, thermo-gravimetric-differential thermal analysis (TG-DTA) of samples was carried out in platinum crucibles using a Setaram, 92-16.18 make TG-DTA instrument. The sample was heated under argon environment up to 1100°C at a heating rate of 10°C/min.