CHAPTER - 2

INSTRUMENTS AND TECHNIQUES USED FOR CHARACTERIZATION
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2.1 INTRODUCTION

In order to confirm the proper preparation and to study different characteristics of the samples, some characterisation techniques were used. The instruments described are X-ray diffraction (XRD) spectrometer, Scanning electron microscopy (SEM), Photoluminescence (PL) spectroscopy, Mechanoluminescence (ML) recorder, Fourier transform infrared (FTIR) spectroscopy, Thermogravimetry, Time resolved photoluminescence (TRPL) decay, and Thermoluminescence reader (TLD). The details of the instruments used for Characterisation and optical studies were elaborated by giving their block diagrams, working principles and formula’s and technical specifications.

2.2 CHARACTERIZATION TECHNIQUES

There is quite large range of Characterisation methods possible for analysis of composition, molecular structure as well as the physical properties of inorganic materials. Few methods are specific for materials composition, molecular structure determination and morphology. In this study we have opted for some Characterisation to determine the molecular structure, morphology, and physical properties like X-ray diffraction, Scanning Electron Microscope images, FTIR (Fourier Transform Infrared) spectra, Differential Thermal Analysis/Thermal Gravimetric analysis and are discussed below:-
2.2.1 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 2.1)

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

Where \( \lambda \) is the wavelength of X-rays, \( \theta \) is glancing angle, \( d \) is inter planar 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 Figure 2.2.1 (a) 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 though 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. [1, 2]

![X-ray diagram](image)

**Fig. 2.2.1 (a) X-Ray diagram of a typical reflection mode diffractometer.**

**Data collection and Analysis:** The output of the diffraction measurement is obtained as a 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 2θ 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 Crystallographic Open Database(COD) files available for reported crystalline samples. The unit cell parameters were refined by a least squares method using the software “Powder X”. The average crystallite size of the phosphor 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 2.2
\[ d = \frac{0.9 \lambda}{\beta \cos \theta} \] ........................ (Eqn.2.2)

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 2.3):

\[ \beta^2 = \beta_M^2 - \beta_S^2 \] ........................ (Eqn.2.3)

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. In the present study, Panalytical Xpert PRO MPD instrument was used for the characterization of all the samples. The Cu-K\( \alpha \) from sealed tube was used as the incident beam. Instrument used for characterisation is shown in Figure 2.2.1 (b):

![Actual Setup of XRD instrument used.](image)

Fig. 2.2.1 (a) Actual Setup of XRD instrument used.
The details of instruments used for XRD is as follows:-

Manufacturer: Panalytical
Model: Xpert PRO MPD
Anode: Copper K-alpha
Wavelength: 1.5405 Angstroms
Power: 45KV and 40mA
Detector: Xcelerator with Diffracted Beam Monochromator

(Tata Institute of Fundamental Research, Mumbai)

2.2.2 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. 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 Figure 2.2.2 (a).

![Schematic representation of SEM microscope.](image)

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 SU 6600-FESEM from Hitachi having standard tungsten filament installed in NIT Calicut, India.
Actual instrument used for SEM analysis is shown in Figure 2.2.2 (b)

![SEM instrument](image)

**Fig.** 2.2.2 (b) SEM instrument used in Lab

The other specifications of the instrument are as shown below:

**THE MAIN FEATURES OF SU 6600-FESEM**

- Electron gun: Tungsten Schottky emission electron source
- Resolution: 1.2 nm/30 kV, 3.0 nm/1 kV
- Probe current: 1pA~200nA
- Specimen chamber pressure : 10-4Pa (high vacuum), 10~300Pa (low vacuum)
- Specimen Size: Max 150 mm dia.×40 mm H
- Magnification: 500,000 x
2.2.3 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. Fluorescence occurs when a molecule absorbs light photons from the UV-Visible light spectrum, known as excitation, and then rapidly emits light photons as it returns to its ground state. Fluorimetry characterizes the relationship between absorbed and emitted photons at specified wavelengths. It is a precise quantitative analytical technique that is inexpensive and easily mastered. All chemical compounds absorb energy which causes excitation of electrons bound in the molecule, such as increased vibrational energy or, under appropriate conditions, transitions between discrete electronic energy states. For a transition to occur, the absorbed energy must be equivalent to the difference between the initial electronic state and a high-energy state. This value is constant and characteristic of the molecular structure. This is termed the excitation wavelength. If conditions permit, an excited molecule will return to ground state by emission of energy through heat and/or emission of energy quanta such as photons. The emission energy or wavelength of these quanta are also equivalent to the difference between two discrete energy states and are characteristic of the molecular structure. Fluorescence occurs when a molecule absorbs photons from the UV - Visible light spectrum (200-900 nm), causing transition to a high-energy electronic state and then emits photons as it returns to its initial state, in less than $10^{-9}$ sec. Some energy, within the molecule, is lost through heat or vibration so that emitted energy is less than the exciting energy; i.e., the emission
wavelength is always longer than the excitation wavelength. The difference between the excitation and emission wavelengths is called the Stokes shift.

The schematic representation of spectrofluorometer can be seen in Figure 2.2.3 (a). 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). [5, 14, 15, 16]
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 monochromator 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 mission 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 2.4.

\[ \eta = \frac{1}{k_r + k_{nr}} \]  

\[ \text{eqn.2.4} \]

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, \( \tau_0 = \frac{1}{k_r} \). 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 be expressed in terms of the radiative lifetime ($\tau_0$) and luminescence lifetimes ($\tau$) by the equation 2.5. \cite{5, 14, 15, 16}

$$\eta = \frac{k_r}{k_r + k_{nr}} = \frac{\tau}{\tau_0} \quad \text{............... (Eqn.2.5)}$$

In the present study all luminescence measurements were carried out by using an Edinburgh Instruments’. In present study the Photoluminescence (PL) excitation & emission spectra were measured by a spectrofluorophotometer (SHIMADZU, RF-5301 PC) using the Xenon lamp as excitation source.

Instrument used in Lab for carrying out Photoluminescence studies is shown in Figure 2.2.3 (b)

![Spectrofluorometer used in Lab](image-url)
The specifications of the instrument used are as follows:

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Source</td>
<td>150W Xenon lamp. Ozone resolving type lamp housing</td>
</tr>
<tr>
<td>Excitation and emission</td>
<td>Concave, blazed holographic grating, F/2.5, 1300</td>
</tr>
<tr>
<td>Monochromators</td>
<td>grooves/mm</td>
</tr>
<tr>
<td>Wavelength Scale</td>
<td>220-990nm</td>
</tr>
<tr>
<td>Wavelength Accuracy</td>
<td>±1.5nm.</td>
</tr>
<tr>
<td>Power requirements</td>
<td>100, 120, 220, 240V; 50/60Hz; 400VA.</td>
</tr>
<tr>
<td>Operational temperature range</td>
<td>15-35°C</td>
</tr>
</tbody>
</table>

### 2.2.4 Mechanoluminescence Study (ML)

In the Figure 2.2.4 (a), (1) stand to hold the load and pulley arrangement, (2) pulley, (3) thread, (4) load, (5) circular cross-sectional tube, (6) Lucite plate, (7) Sample, (8) Lucite plate holder, (9) Box to cover Lucite plate arrangements, (10) Photomultiplier tube, (11) Stand

A particular load is tied at the top using pulley & thread as shown in figure which is made to fall on the sample which is placed on a Lucite plate. When the load strikes the sample, it starts to deform in shape, which causes Mechanoluminescence and a light comes out of the sample suffering the force of the load. The intensity of the light is measured by using photomultiplier located near to the Lucite plate and is recorded in oscilloscope. For plotting the curve between Stresses – Intensity, we change the weight of the load and record the intensity. [6]

One another method to measure the ML is to change the height of the fixed load striking the sample, by which we will be able to calculate the velocity at which the
load is striking so we may be able to plot another ML Characteristics between velocity and intensity. [6, 7, 8]

Fig. 2.2.4 (a) Experimental arrangements of ML measuring device

Fig. 2.2.4 (b) ML measuring device used in Lab

The Instrument used to carryout Mechanoluminescence Studies is shown in Figure 2.2.4 (b).
2.2.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR Imaging is a complimentary Imaging tool and is a very versatile analytical technique for spectrochemical imaging. The advantage of chemical imaging compared to other sensor technologies is the ability to analyze the spatial distribution of the component materials in blends, granules or finished dosage forms. Many analysts need to obtain the molecular information from an area of a sample to see a picture of the distribution of molecules or functional groups. These chemical pictures called IR images provide information that is highly complementary to images obtained from techniques such as Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and visible light microscopy. SEM and AFM have each a much higher spatial resolution than FTIR imaging, down to less than 1 nm. These techniques provide information about surface properties and in some cases, elements distribution, but they do not provide information about molecular composition. The chemical imaging approach has the potential to monitor processes to reveal the extent of ingredient blending, particle size distributions, agglomeration of component particles and the presence of polymorphs, hydrates and other trace contaminants. [9]

Fourier Transform Infra-Red (FTIR) Spectroscopy is well proven as a sensitive, rapid technique for material characterization of various samples for molecular species in a broad range of materials. By coupling the FTIR to a microscope accessory, measurements on small sample can be routinely carried out, down to few micron areas. Applications include the identification of trace contaminants, the analysis of failure modes and characterization of production defects. [9-10]
Both FT-IR and FT-NIR take advantage of the fact that the functional groups of every module generate a characteristic absorption or transmission spectral fingerprint that definitely identifies that chemical compound. FTIR and FT-NIR are quickly becoming the preferred compound testing technologies because of their speed, accuracy and reliability. While infrared microscopy provides the highest sensitivity and widest spectral range for small area FTIR measurements, collecting microscopic chemical picture of your sample can be time consuming, depending on the data collection and sample size requirements. Unlike IR microscopes that employ a single detector measuring a single point at a time, FTIR imaging systems contain multi-element detectors, producing IR images almost as fast as an optical microscope presents a visible image.\[9-10\]

**Dispersive IR Spectrometers**

Beam from an IR source is split into two halves using a mirror. One beam is passed through a reference cell; the other is passed through a sample cell. The two beams are alternately passed to the diffraction grating using a beam chopper. Absorption of radiation is detected by comparing the two signals Light is dispersed (spread into constituent wavelengths) by a grating much as it would be by a prism. The grating is slowly rotated, which changes the angle if diffraction and which wavelengths are passed to the detector.\[11-12\]

Figure 2.2.5 (a) expresses the experimental arrangement for recording FT-IR Spectrum. Spectrum recorded in the frequency domain
Fig. 2.2.5 (a) Experimental arrangement of FTIR
Sample Preparation for IR Work

Three major methods of sample preparation

1. Sample is mixed with a mulling agent such as mineral oil and pressed between plates made of sodium chloride. Sodium chloride is used because it has no IR absorptions; glass or plastic plates would have IR absorptions of their own. Sodium chloride plates are good from 4000 to 650 cm\(^{-1}\); below 650 cm\(^{-1}\) they begin to absorb. Potassium bromide plates can be used in place of sodium chloride and are transparent to 400 cm\(^{-1}\), but they are more expensive.

2. Sample is mixed with solid potassium bromide and pressed into a pellet under high pressure. No absorptions from mulling agent.

3. Solids Sample is dissolved in carbon tetrachloride and pressed between salt plates.

Figure 2.2.5 (b) shows the instrument used for FTIR studies in Laboratory

Fig. 2.2.5 (b) FTIR Instrument used
Specifications of the instruments used for FT-IR in IIT Mumbai are as follows:

- Make: Bruker, Germany
- Model: 3000 Hyperion Microscope with Vertex 80 FTIR System.
- Focal plane array: 128 x 128 range: 4000-900 cm\(^{-1}\).
- Single point detector: range: 7500-450 cm\(^{-1}\)
- Spectral resolution of FTIR 0.2 cm\(^{-1}\)
- Rapid scan & step scan available. Rapid scan 65 spectra/sec at 16 cm\(^{-1}\)

### 2.2.6 Differential Thermal Gravimetry/Thermogravimetry (DTA/TG)

The instrument used in thermogravimetry (TG) is called a thermobalance. It consists of several basic components in order to provide the flexibility necessary for the production of useful analytical data in the form of TGA Curve as shown in Fig. 2.2.6.

Basic components of a typical thermobalance are listed below: [13]

i) Balance
ii) Furnace: heating device
iii) Unit for temperature measurement and control (Programmer)
iv) Recorder: automatic recording unit for the mass and temperature changes

These components may be represented by simple block diagram as in Fig. 2.2.6.1
Fig. 2.2.6.1 Block diagram of a Thermobalance

(i) Balance

The basic requirement of an automatic recording balance are includes accuracy, sensitivity, reproducibility, and capacity. Recording balances are of two types, null point and deflection type. The null type balance, which is more widely used, incorporates a sensing element which detects a deviation of the balance beam from its null position; a sensor detects the deviation and triggers the restoring force to bring the balance beam to back to the null position. The restoring force is directly proportional to the mass change. Deflection balance of the beam type involve the conversion of the balance beam deflection about the fulcrum into a suitable mass change trace by (a) photographic recording i.e. change in path of a reflected beam of light available of photographic recording, (b) recording electrical signals generated by an appropriate displacement measurement transducer, and (c) using an electrochemical device. The different balances used in TG instruments are having measuring range from 0.0001 mg to 1 g depending on sample containers used. [13-15]
(ii) **Furnace**

The furnace and control system must be designed to produce linear heating at over the whole working temperature range of the furnace and provision must be made to maintain any fixed temperature. A wide temperature range generally -150 °C to 2000 °C of furnaces is used in different instruments manufacturers depending on the models. The range of furnace basically depends on the types of heating elements are used. [13-15]

(iii) **Temperature Measurement and Control**

Temperature measurement are commonly done using thermocouples, chromal-alumel thermocouple are often used for temperature up to 1100 °C whereas.

(iv) **Recorder**

Graphic recorders are preferred to meter type recorders. X-Y recorders are commonly used as they plot weight directly against temperature. The present instrument facilitate microprocessor controlled operation and digital data acquisition and processing using personal computer with different types recorder and plotter for better presentation of data. [13-15]

A schematic diagram of the specific balance and furnace assembly as a whole is shown in Figure 2.2.6.2 to better understand the working of a thermobalance. In this diagram, it can be seen that the whole of the balance system is housed in a glass to protect it from dust and provide inert atmosphere. There is a control mechanism to regulate the flow of inert gas to provide inert atmosphere and water to cool the furnace. The temperature sensor of furnace is linked to the programme to control
heating rates, etc. The balance output and thermocouple signal may be fed to
recorder to record the TG Curve.

**Fig. 2.2.6.2** Schematic diagram of a typical balance and furnace assembly

**Thermogravimatic Curves**

So far we have discussed the instauration of TG now we turn our attention to
quantitative aspects of TG. As discussed earlier TG curves represent the variation in
the mass \( m \) of the sample with the temperature \( T \) or time \( t \). Normally, we plot
mass loss downward on the ordinate \( y \) axis and mass gain upwards as shown in
Fig.2.2.6.3.
Thermal Methods

Fig. 2.2.6.3  TG Curve. Note the plateau of constant weight (region A), the mass loss portion (region B), and another plateau of constant mass (region C)

Sometime we also record derivative thermogravimetric (DTG) Curves. A DTG curve presents the rate of mass change ($\frac{dm}{dt}$) as a function of temperature, or time ($t$) against $T$ on the abscissa ($x$ axis) as shown in Fig. 2.2.6.3 when substance is heated at uniform rate. In this figure, the derivative of the Curve is shown by dotted lines. [15-17]
Specifications of the instrument used for DTA/TG in this study are as follows:

Temperature Range: Ambient to 1500°C

Balance type: Horizontal Differential type TG measurement Range/ Sensitivity: 200 mg /0.2μg

DTA measurement / Sensitivity: +1000μV/ 0.06μV

Programmable Heating Rate: 0.01 to 100°C/Minute

Sample Pan Material: Platinum, Aluminum and Alumina

Sample Pan Volume: 45μL

Atmosphere: Air, Inert Gas

Purge Gas Flow Rate: 0 to 1000 ml/Minute

2.2.7 Measuring Afterglow of a phosphor

Persistency of a phosphor is judged by the amount of time during which any phosphor glows after the excitation source is removed. For achieving this, we are supposed to
note down the value of emission intensity with respect to time. Sometimes it is not possible to measure the emission intensity for whole lifetime of the phosphor because it may last till few hours also and even after that the optical intensity doesn’t reach to zero. So we used to plot a graph between emission intensity and time then calculate the decay constant to identify the phosphor with optimum afterglow capabilities.

A schematic representation of a setup used for decay recording is shown in Figure 2.2.7 (a), Ultraviolet wave of 365 nm was used for excitation. This UV radiation is applied to the sample results in emission of radiation in visible range. A photomultiplier tube (PMT) is able to sense this radiation and convert this into electrical signals. For amplifying this signal an Extra High Tension power supply with 700 V is connected to PMT. Output of PMT is recorded by the Digital Micro/Nano ammeter.

Experiment setup prepared for measuring the same is illustrated in Figure 2.2.7 (b). An UV of 365 is applied to the sample for 1 minute which produced emission of specific wavelength. The sample is placed above transparent Lucite plate. Finally the emitted light enters photomultiplier tube (PMT). The signal is amplified and creates a current that is proportional to the measured emitted intensity. Output current is measured with the help of Digital Micro/Nano Ammeter.
**Fig. 2.2.7 (a)** Block diagram for Experimental Setup to record afterglow

**Fig. 2.2.7 (b)** Experimental Setup to record afterglow
2.2.8 Thermoluminescence Glow Curve Analysis

The glow curve is a curve between temperature and thermoluminescence intensity. The schematic arrangement of typical thermoluminescence experimental setup is shown in Figure 2.2.8 (a) expresses that the sample is placed in a Nichrome/Canthol heater plate which is heated using thermocouples with temperature control facility. The pre-exposed sample is placed on the Nichrome plate which is heated up, which results in the emission of light from the sample that emitted light is then approaches to the photomultiplier tube (PMT) via blue filter and light guide then after amplifying the signal we get the glow curve in X-Y plotter. [18-19]

Fig. 2.2.8 (a) Schematic diagram to show the experimental setup of TL measurements
In present study we used Computerized TL Setup supplied by Nucleonix (Hyderabad, India) I-1009 TLD reader (Figure 2.2.8 (b)),

![Laboratory setup for TL measurements](image.png)

**Fig. 2.2.8 (b) Lab setup for TL measurements**

The specifications of instrument used for TL measurement is as follows:-

- **Heating rates are:** $1^\circ$C/sec to $40^\circ$C/sec
- **Max. Set temperature:** $500^\circ$ C
- **Heating profile:** Linear, plateau heating (One/Two/Three)

Software features include glow curve, acquisition, display, filing, printing, processing over lapping Area under peak, subtraction etc.
REFERENCE


