Experimental techniques

This chapter explains the various experimental techniques employed for the preparation, characterization and property measurement of the samples under investigation.

2.1 Materials

The following chemicals of analar or equivalent grade chemicals were used.

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Chemical name</th>
<th>Chemical formula</th>
<th>Make</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Silver nitrate</td>
<td>AgNO₃</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>2</td>
<td>Zinc nitrate</td>
<td>Zn(NO₃)₂</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>3</td>
<td>Cerium nitrate</td>
<td>Ce(NO₃)₃</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>4</td>
<td>Gadolinium nitrate</td>
<td>Gd(NO₃)₃</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>5</td>
<td>Europium nitrate</td>
<td>Eu(NO₃)₃</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>6</td>
<td>Sodium phosphate buffer</td>
<td>NaH₂PO₄</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>7</td>
<td>Nitric acid</td>
<td>HNO₃</td>
<td>BDH</td>
</tr>
<tr>
<td>8</td>
<td>Ethanol</td>
<td>C₂H₅OH</td>
<td>Qualigens</td>
</tr>
<tr>
<td>9</td>
<td>Acetone</td>
<td>C₃H₆O</td>
<td>Qualigens</td>
</tr>
</tbody>
</table>

2.2 Physico-chemical (characterization) techniques

2.2.1 Powder X-Ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) is a versatile, non-destructive analytical method for identification and quantitative determination of various crystalline forms, known as ‘phases’ of compound present in powder and solid samples. Diffraction occurs as waves interact with a regular structure whose repeat distance is about the same as the wavelength. The phenomenon is common in the natural world and occurs across a broad range of scales. For example, light can be diffracted by a grating having scribed lines spaced of the order of a few thousand angstroms, about the wavelength of light. It happens that X-rays have wavelengths about a few angstroms, the same as typical inter-atomic distances in crystalline solids. That means X-rays can be diffracted from minerals, which, by definition, are crystalline and have regularly repeating atomic structures. When
certain geometric requirements are met, X-rays scattered from a crystalline solid can constructively interfere, producing a diffracted beam. In 1912, W. L. Bragg recognized a predictable relationship among several factors, namely

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

b. 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'.

c. The wavelength of the incident X-radiation, symbolized by the Greek letter lambda and in our case, equal to 1.54 angstroms.

\[ n\lambda = 2d \sin \theta \] (Bragg’s law)  
\[(2.1)\]

where \( \lambda \)- wavelength of X-ray, d-interplaner spacing, \( \theta \)-diffraction angle, \( n=0,1,2,3,\ldots \)

Here PXRD was done by the X-ray diffraction of the as milled powder samples were performed using the diffractometer. X-Ray diffraction patterns were recorded from 10° to 80° with a PANalytical X’Pert Pro diffractometer using Cu Kα (\( \lambda=1.542\text{Å} \)) with nickel filter. Data were collected with a counting rate of 2° per min (Fig.2.1).

### 2.2.1.1 Particle size measurement from the line broadening in PXRD

There are various factors, which affect the broadening of diffraction peaks namely (i) crystalline domain size (ii) domain size distribution (iii) crystalline facets (external defects) and microstrain (deformation of the lattice), etc.
The crystalline size ($d$) was estimated from the broad PXRD peaks using the Scherer’s method [1].

$$d = \frac{K\lambda}{\beta \cos \theta} \quad (2.2)$$

where $d$; the average grain size of the crystallites, $\lambda$; the wavelength of the CuK$_\alpha$ (1.54 Å), $\theta$; the angle between the incident beam and the reflection lattice planes and $\beta$; the full width at half maxima (FWHM) of the diffraction peak in radian. $K$ ; a constant (shape factor) depends on the grain shape. The value of $K$ can vary 0.7 to 0.9 depending on the crystalline shape. Klug and Alexander [1] suggest the use of 0.9 for calculating average crystallite diameter for circular shaped particles.
Further the broadening of PXRD peaks are due to microstrain, which is proportional to the \( \tan \theta \). Thus, we can obtain the Williamson-Hall (W-H) formula [2] by combining the effect on powder X-ray diffraction patterns for broadening

\[
\beta \cos \theta = \frac{0.9\lambda}{D} + 4\varepsilon \sin \theta
\]  

(2.3)

where \( \varepsilon \); the strain associated with the nanorods. Equation (2.3) represents a straight line between \( 4 \sin \theta \) (X-axis) and \( \beta \cos \theta \) (Y-axis). The slope of line gives the strain (\( \varepsilon \)) and intercept (\( 0.9\lambda/D \)) of this line on Y-axis gives crystallite size (D).

### 2.2.1.2 Rietveld refinement

Until 1970 powder diffraction was viewed primarily as a tool for phase identification and quantitative analysis. Its use for structure refinement was limited to simple systems because of severe peak overlap. H. Rietveld (1967) came up with a new approach to extract maximum crystal structure information from powder diffraction data using the method of least squares [3]. The introduction of Rietveld method has greatly enhanced the use powder diffraction data for structure refinement and has provided a major boost to structure solution from powder data in a systematic way [4]. The development of Rietveld method for refining crystal structures, first from neutron powder diffraction data and later from X-ray diffraction data has resulted in a wide application of this method to almost every hot areas of research from complex oxides, zeolites, organic molecules and most recently to polymers and proteins [3]

In Rietveld refinement of a crystal structure from powder diffraction data, every observation in the powder diffraction profile is considered as intensity measurement. The powder diffraction profile is calculated using the following information: (i) background intensity, (ii) lattice parameters and space group (peak positions), (iii) atomic positions
and atomic displacement parameters (peak intensities), (iv) \(2\theta\) dependent analytical function (peak shapes and peak width) and occupation factors.

For Rietveld refinement, the powder data must be collected accurately in digitized form using a properly aligned and calibrated diffractometer. Factors such as suitable radiation (e.g. conventional X-rays, synchrotron X-ray or neutron), the wavelength, diffractometer geometry (e.g. Debye-Scherrer, Transmission, Bragg-Brentano), sample preparation, step-scan increments, counting time etc, must be evaluated carefully based on the characteristics of the sample under study before collecting the data.

The model-parameters that may be refined include not only positional, thermal and site occupancy of the atoms in the starting structural model but also parameters for the background, lattice, instrumental geometrical-optical features, specimen aberrations (e.g. specimen displacement and transparency), an amorphous component and specimen reflection-profile-broadening factors (e.g. crystallite size and micro strain). Multiple phases may be refined simultaneously for quantitative phase analysis.

The criteria for the best fit are based on the several \(R\) factors, developed from the well established single crystal diffraction methodology. The various \(R\) factors include, \(R_p\) - R profile, \(R_{wp}\) – R weighted profile, \(R_b\) – R Bragg factor, etc. the Rietveld refinement can be terminated as soon as the model is well refined. This can be seen when best fit is obtained between observed and calculated powder diffraction patterns and the changes in the individual parameters are no longer significant [3, 5].
In the present study, the Rietveld refinement was performed through the FULLPROF program [6-8]. We utilize the psedo-voigt function in order to fit the several parameters to the data point: one scale factor, one zero shifting, four background, three cell parameters, five shape and width of the peaks, one global thermal factor and two asymmetric factors. The packing diagrams of corresponding samples were obtained after Rietveld refinement. The refined parameters such as occupancy, atomic functional positions volume and R$_f$ factors are obtained.

2.2.2 Scanning electron microscopy (SEM)

Electron microscopy is a versatile tool capable of providing structural information over a wide range of magnification. Electron microscopes are of either transmission or reflection design. Transmission and scanning electron microscopes together offer an important tool for the characterization of materials. Scanning electron microscopy (SEM) is mainly employed to study the texture, topography and surface features of powders or solid pieces. During SEM inspection, a beam of electrons is focused on a spot volume of the specimen, resulting in the transfer of energy to the spot. These bombarding electrons, also referred to as primary electrons, dislodge electrons from the specimen itself. The dislodged electrons, also known as secondary electrons are attracted and collected detector and then translated into a signal. To produce the SEM image, the electron beam is swept across the area being inspected, producing many such signals. These signals are then amplified, analyzed and translated into images of the topography under study. Finally, the image is shown on a cathode ray tube (CRT). In the present study FEI Quanta 200 scanning electron microscope (Fig. 2.2) was used to study the morphology of the samples.
2.2.3 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is used to obtain information from samples that are thin enough to transmit electrons. In TEM the whole area of interest is illuminated simultaneously. An electron source is required which can produce large total current, so that whole region of interest is illuminated at a useful intensity, even when examining at magnifications of 100x or less. The transmitted electrons are generally used to form either an image or a diffraction pattern of the specimen. The diffraction lens (the lens immediately after the objective lens) is focused on the plane where image is formed by the objective lens. Subsequent lenses are used to magnify this further and hence a highly magnified image can be formed on the final screen. In the diffraction lens is focused on the plane where the objective lens forms a diffraction pattern. Again the lenses below the diffraction lens are used to magnify further the diffraction pattern. There are two different ways of obtaining images of sample in TEM: a) conventional imaging and b) high resolution imaging. First method involves the use of an aperture in the back focal plane, which allows only one electron beam to contribute to the image. This method of obtaining image information therefore exclude the possibility of observing the periodicity.
of crystalline samples, since interference of at least two beams are required in the image plane to obtain such periodic information and contrast arises either from diffraction contrast or phase contrast. The second method of obtaining an image also involves the use of an aperture, but in this case the direct beam and a number of diffracted beams are allowed to contribute to the image. When using the microscope in the conventional image mode, the objective aperture is used to select only one electron beam to form the image. A bright field image is formed in directly transmitted beam is selected and a dark field image is formed if a diffracted beam is selected. If the crystal has been set up in such a way that only one strong diffraction beam is excited, then this beam is selected for imaging. This technique is usually used when crystal defects are imaged. A diffraction pattern is formed in the back focal plane of the objective lens. Hence if the diffraction lens is focused onto the back plane of the objective lens, rather that on to the first image plane and objective aperture is removed, the diffraction pattern will be visible on final screen. There are two methods which are commonly available a) selected area electron diffraction (SAED) using an aperture to select the area b) selected area diffraction using a focused electron probe to define the selected area.

The first method is used in conjunction with a defocused electron beam so that a large area of the sample is illuminated with electron and hence this large area is contributing to the generation of diffraction of beams. The technique involves inserting an aperture in the first image plane so that only those electrons generated from the area defined by the aperture will be able to contribute to the diffraction pattern. The other technique simply involves condensing the electron probe to the area of interest, so that the probe position uniquely define the region from where the diffraction beam originates. The electron probe mode is the most common method of obtaining the diffraction pattern. In
the present study the Hitachi H-8100 (accelerating voltage up to 200 kV La B6 filament) and equipped with an ultra high resolution objective pole piece in the top entry configuration was used (Fig. 2.3). The cleaved samples are examined under the transmission electron microscope in order to study the nature of the defect (dislocation) structure and the inter planar spacing. The SAED patterns are also obtained in certain cases.

2.2.4 Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy is sensitive to lattice mode thus FTIR is an important and appropriate mode for oxide materials in which lattice parameter play an important role. The intensities of the FTIR bands provide a good measure of the electronic properties of the oxides. In the present study Perkin Elmer FTIR spectrometer, (spectrum 1000) with KBr pellets was used to study the FTIR of as-formed and calcined samples (Fig. 2.4).
2.2.5 Ultra Violet Visible (UV-Visible) absorption spectroscopy

Ultra Violet Visible (UV-Visible) absorption spectroscopy investigates the interactions between ultraviolet or visible electromagnetic radiation and matter. UV-Visible spectroscopic measurements provide precise information about molecular species present in the sample. In the present study, the UV-Visible absorption of the samples was recorded on SL 159 ELICO UV-VIS Spectrophotometer (Fig. 2.5).

SL 159 Scanning UV-Visible Spectrophotometer consists of the followings

- Microprocessor based with Printer Interface.
- Optional PC compatibility with RS 232C Interface.
- Automatic 6 position holder.
- 21 CFR PART 11 Compliant Software.
2.2.6 Photoluminescence (PL) spectroscopy

When light strikes a phosphor in the ground state, it absorbs radiation of certain specific wavelength to jump to an excited state. A part of the excitation (absorbed) energy is lost on vibration relaxation, i.e., radiationless transition to the lowest vibrational level takes place in the excited state and eventually it returns to the ground state by emitting energy, which is called fluorescence. Fluorescence continues for a period of $10^{-8}$ to $10^{-9}$ sec in most cases. Since a part of the radiation absorbed is lost, the fluorescence emitted from the substance has a longer wavelength (lower energy) than the excitation radiation (Stokes’ law).

The emission transition occurring in a solid is seen as a glow and is registered in the form of a band in the luminescence spectrum. The position of the band in the luminescence spectrum does not depend upon the method of excitation. The luminescence spectra are normally observed with the intensity of luminescence as a function of the emission wavelength. The same instrument can be used to measure the spectral distribution of luminescence (emission spectrum) and the vibration in the emission intensity with excitation wavelength (excitation spectrum) or with activator concentration.
Photoluminescence (excitation and emission) spectra were recorded using Jobin Yvon Spectroflourimeter Fluorolog-3 equipped with 450 W Xenon lamp. Fig. 2.6 depicts the block diagram of the experimental set-up used to record the luminescence spectrum of phosphor sample. The light emitted from the Xe-lamp enters the excitation monochromator. The light emerging from the excitation monochromator is split by the beam splitter and a fraction is directed to the monitor detector. All the driving component i.e., the wavelength drive motors and slit control motors are operated by signal sent from the computer. On the other hand. Output signal from the monitor detector and fluorescence detector (photomultiplier) are processed by the computer via the A/D converter transmitted to the CRT or graphic plotter.

In the present investigations photoluminescence (PL) was performed on a Horiba Spectrofluoremeter (Model Flurolog-3) equipped with 150 W Xenon lamp as an excitation source (Fig. 2.7).
Fig. 2.6. Block diagram of the photoluminescence spectrometer used.
2.2.7 Photocatalytic Activity

Photodegradation of Methylene blue dye (Table 2.1) was done with pure ZnO, and Eu$^{3+}$ doped ZnO. Methylene Blue of $1 \times 10^{-3}$M was prepared as stock solution in a 100 mL flask.

Table 2.1 Physical and molecular characteristics of Methylene Blue.

<table>
<thead>
<tr>
<th>Dye name</th>
<th>Methylene Blue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suggested name</td>
<td>Methylene Blue</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>MB</td>
</tr>
<tr>
<td>C. I. name</td>
<td>Basic Blue 9</td>
</tr>
<tr>
<td>C. I. number</td>
<td>52015</td>
</tr>
<tr>
<td>Class</td>
<td>Thiazine</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>664 nm</td>
</tr>
<tr>
<td>color</td>
<td>Blue</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C$<em>{16}$H$</em>{18}$N$_3$SCl</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>319.9 g/mol</td>
</tr>
<tr>
<td>Molecular Volume (cm$^3$/mol)</td>
<td>241.9</td>
</tr>
<tr>
<td>Molecular diameter (nm)</td>
<td>0.8</td>
</tr>
<tr>
<td>Molecular Structure</td>
<td></td>
</tr>
</tbody>
</table>
Necessary dilutions of this stock were done with deionized water. A given amount of the catalyst (ZnO ~ 50 mg) was added to 100 mL of this diluted solution (Methylene Blue = $1 \times 10^{-5}$ M). The contents of the dye solution were allowed to equilibrate for a given time (usually 30 – 60 min) in the dark before irradiation. The samples were then irradiated with a UV lamp in a photochemical reactor.

The photochemical set up was made up of a double jacketed quartz tube of 3.4 cm internal diameter and 21 cm length. A high pressure mercury vapour lamp of 125 W was placed inside the double jacketed quartz tube (Fig. 2.8). To avoid fluctuations in the input, supply ballast and a capacitor were connected in series with the lamp. Water was circulated through the annulus of the quartz tube to avoid heating of the solution. During irradiation, the contents of the solution were agitated continuously so as to maintain a homogeneous environment.

Fig. 2.8. UV irradiation set up.
After a certain time interval, the cell was drawn away from the UV light and centrifuged and the absorbance of the supernatant solution was monitored instantaneously on a UV Visible spectrometer. The absorbance value obtained in each case was plotted against time to obtain the rate of decoloration. UV-Vis studies were done on a Perkin Elmer UV-Vis spectrophotometer, using a 1cm quartz cell. Absorbance measurements were recorded in the range of 200 – 800 nm, and the maximum absorption wavelength experimentally registered at $\lambda = 664$ nm for the dye (MB) was used for the calibration curves and further concentration measurements.
References


