Chapter 2
Instrumentation

Introduction

In materials science, characterization refers to the broad and general process by which a structure of material and its properties are probed and measured to ascertain the quality of material. The quality of these materials can be evaluated by the size of the crystallites, single-phase material or preferred orientation using a particular technique and to continue further studies of the electrical, magnetic and optical properties of the materials.

The techniques used for the characterization and analysis of the synthesized materials include X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy – Dispersive X-ray Spectroscopy (EDAX) and NIR spectroscopy for Up-conversion Photoluminescence measurements.

2.1 X – ray Diffraction (XRD)

XRD is a tool used for identifying the atomic and molecular structure of a crystal. A crystal consists of a set of parallel atomic planes. When a beam of X-rays is incident on the crystal, these rays get scattered in specific directions. The phenomena of scattering is general to all waves and can be also defined as the interaction of the waves with an object leading to modification of the behavior of the interacting light or other waves. In the case of interaction of X rays with a crystal, the scattering is in terms of diffraction. The wave encounters a series of regularly spaced atomic planes with spacings that are comparable in magnitude to the wavelength of X rays [1]. This is shown in the figure below.

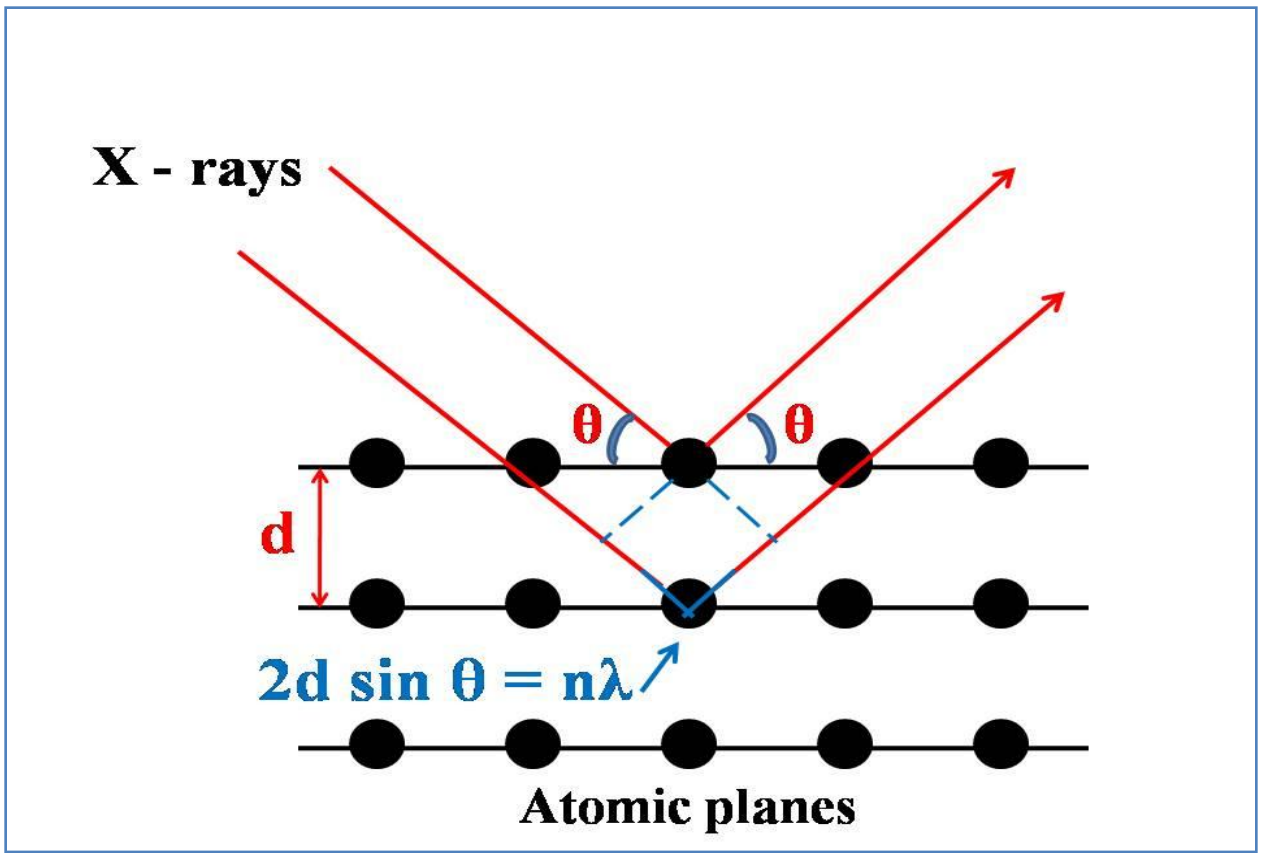

Figure 2.1: Reflection of X-rays by two successive atomic planes

The path difference between the two successive atomic planes with spacing d becomes an integral multiple of the wavelength λ of the incident radiation at specific angles θ. The relations between these parameters is given by the Bragg's Equation,

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

where n is an integer, corresponding to the order of diffraction from the crystal planes which acts as a grating. Hence, nλ is the path difference between the scattered waves.

Each crystalline solid has its unique characteristic XRD pattern which may be used as a "fingerprint" for its identification. Once the material is subjected to X-ray analysis, the obtained data is analyzed to identify the crystal structure and determine the unit cell parameters using standard sources like JCPDS and ASTM or by Rietveld Refinement [2].

Identification of the phases was carried by comparison with the Joint Committee for Powder Diffraction Standards (JCPDS) files [3]. The crystallite size was estimated by using the Scherer formula [4].

$$D = \frac{K\lambda}{\beta \, Cos \, \theta}$$

where D is the crystallite size, K is a constant equal to ~ 0.9, λ is the X ray wavelength, β is the full width at half maximum (FWHM) and θ is the Bragg angle of the peak .

The XRD patterns in this study were recorded on a X'Pert Pro PANaytical Powder Diffractometer with Cu-Kα radiation source (λ = 1.54 Å) operated at 40 kV and 40 mA in the 2Θ range 20 – 80 degree at the scan speed of 0.05 degree per second.

2.2 Scanning Electron Microscopy (SEM) and Energy – Dispersive X-ray Spectroscopy (EDX)

The structure of material can be also studied by using optical microscope or by transmission electron microscopy. This is done by passing electrons through a thin specimen and imaging it. In the scanning electron microscopy, the imaging is done by collecting electrons emitted from the surface of the specimen [5]. It produces a largely magnified image by using electrons instead of light to form an image.

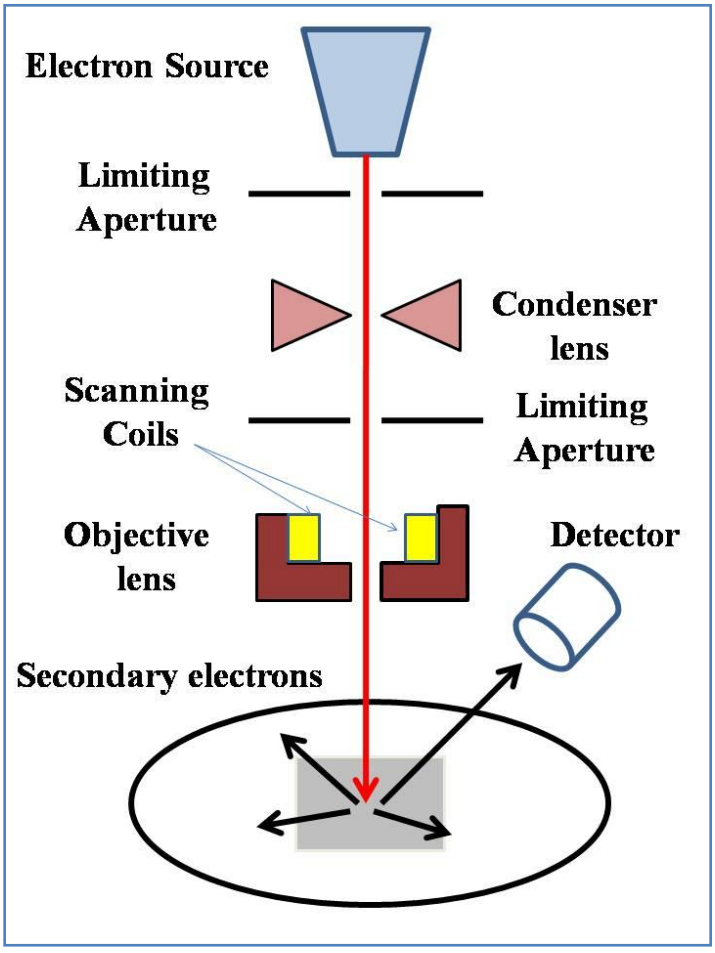

Figure 2.2: A schematic view of SEM

A schematic view of SEM is as shown in the figure 2.2. The electrons are emitted by a source, which is generally a Tungsten filament. These electrons and accelerated by a potential of tens of kilo volts. The electron beam is collimated by an electromagnetic condenser lens and made to pass through a column. The beam is then passed through deflection coils to produce the deviation of the electron beam for scanning the sample.

The interaction between the electron beam and the sample generates X-rays, backscattered electrons, Auger electrons and secondary electrons. All of these provide valuable information about the sample.

The secondary electrons are the only ones which have probability to escape from the surface of the specimen. These electrons are used for image construction. They are detected by a scintillation counter and amplified by the photo-multiplier tube to obtain the signal output. The obtained signal is correlated with scanning point to form the image. This image shows the topography with good contrast.

The other signal from the sample is characteristic X-rays. Characteristic X rays are produced when the accelerated electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays provide quantitative information about the composition of samples in terms of elements present in the sample. X-ray analysis is a commonly feature found in modern SEM which is referred to as Energy Dispersive X-ray analysis.

It has been accepted as a standard procedure for indentifying and quantifying elemental composition of specimen surfaces at shallow depths, as small as few micrometers. A separate unit called energy dispersive X-ray Spectrometer (EDAX) is coupled to the SEM. It provides a chemical microanalysis of the sample.

SEM images of the synthesized samples were taken with a JEOL make MODEL JSM 5810 LV and the quantitative elemental composition analysis was carried out by energy dispersive X – ray spectroscopy (EDAX) system equipped with the SEM machine.

2.3 NIR Spectroscopy for Up-conversion Photoluminescence Measurements

Photoluminescence is the generation of light by a material on excitation by photons. These photons may range in energy from ultraviolet to infrared. The emission characteristics provide vital information. The study is often referred as fluorimetric analysis and the instrument is called.

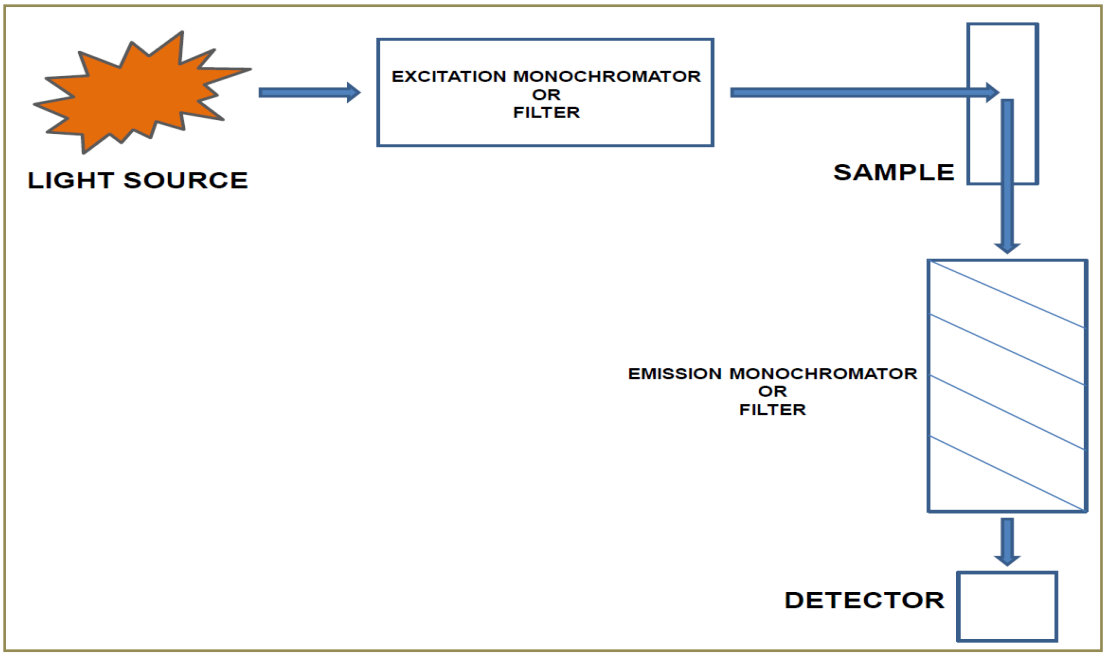

Figure 2.3: A simple view of essential components of Fluorescence Spectrometer

The fluorescence spectrometer primarily has a source of light, monochromators, a sample holder and a detector. The monochromators enable the wavelength of incident and emitted radiation to be selectable. The detector signal is capable of precise manipulation and presentation.

The process of fluorescence consists of excitation and emission. The sample is subjected to a narrow and specific portion of the spectrum, which is absorbed in about 10^{-15} Sec [6].

The fluorescence emission spectrum must be determined before the wavelength for the measurements of the fluorescence can be selected. A precise list of components is given below

1) Xenon arc-lamp and Lamp Housing
    1a) Xenon-lamp Power Supply
    1b) Xenon flash lamp
2) Excitation monochromator
3) Sample Compartment
4) Emission monochromator
5) Signal Detector (Photomultiplier tube and Housing)
6) Reference Detector (Photodiode and Current-Acquisition module)
7) Instrument Controller (Host Computer)

The excitation source generally is a 150 W Ozone free Xenon arc-lamp. Light from the lamp is collected is focused on the entrance slit of the excitation monochromator. A quartz window is used to separate the lamp housing from the excitation monochromator. This prevents lamp failure by venting the heat out of the instrument and provides protection. The installed software controls the entry and exit sections of the monochromators using adjustable slits. The width of the slits on the excitation monochromator determines the band pass of light incident on the sample. The slits on the emission monochromator control the intensity of the fluorescence signal recorded by the signal detector.

An excitation shutter is provided just after the excitation monochromator's exit slit which protects samples from photo degradation from prolonged exposure to the light source. An emission shutter is an optional accessory placed just before the emission monochromator's entrance which protects the detector from bright light. A toroidal mirror focuses the beam from the excitation monochromator on the sample. Emission from the sample is then collected and directed to the emission monochromator. The sample compartment accommodates various optional accessories as well as fiber optic bundles to take the excitation beam to the sample and return the emission beam to the emission monochromator.

For an up conversion set up, the 150 W Xenon arc lamp is replaced by a 980 nm infrared laser diode, which is used as a excitation source. The up-conversion luminescence study for this work was carried out by using confocal photoluminescence mapping system (alpha 300 M+) – WItec Co. at National Physical Laboratory, Delhi.

2.4 References

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[6] H. H. Williard, L. L. Merritt Jr, J. H. Dean, Instrumental Methods of Analysis, 4th Edition, New Jersey, 1965.