Chapter 2

Experimental Techniques
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Abstract

In this chapter, the details of various experiments carried out in this dissertation are explained. We also describe the different experimental techniques namely, X-ray powder diffraction, Fourier Transform Infrared (FTIR), micro-Raman, Absorption, Electro Paramagnetic Resonance (EPR) spectroscopy, Field emission scanning electron microscope (FESEM) with energy dispersive X-ray absorption spectroscopy (EDXAS), Transmission electron microscope (TEM), and Z-scan that form the basis of the studies presented in this thesis.
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The present chapter gives a brief description of different experimental techniques used in the present study. Very brief details of X-ray powder diffraction, Thermogravimetric analyzer (TGA), UV-Vis, FTIR, Raman, FE-SEM-EDAX, TEM and Z-scan experimental facilities used are given below.

2.1 X-Ray Diffraction (XRD)

X-ray Diffraction (XRD) is an analytical technique with a very broad range of applications in physics, materials science, geology, mineralogy, ceramics, etc. The powder diffraction is characteristic of the substance and forms a sort of fingerprint [1] of the substance and yield a great deal of structural information about the crystalline materials. Powder diffraction method involves the diffraction of monochromatic X-rays by a powder specimen. Monochromatic usually means a strong Kα characteristic component of the filtered radiation from X-ray tube operated above the Kα excitation potential of the target material. INEL X-ray diffractometer with Co target X-ray tube is used for the X-ray diffraction measurements. Position Sensitive Detector (PSD) filled with P10-gas (10% methane in Argon) is employed to record the counts.

The peaks of the X-ray diffraction pattern of the synthesized powders samples are compared with a standard available data for confirmation of the structure. We have used the standards like Willars Hand book, Joint Committee on Powder Diffraction Standards (JCPDS) Pcpdf win and National Bureau of Standards among the many available in the literature [2].

If the material under investigation is crystalline, then well-defined peaks will be observed while non-crystalline or amorphous systems show a hallow instead of well defined peaks. In X-ray diffraction the line broadening is caused by small crystallite size, the crystallite size can be estimated from the Scherrer's equation
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d=k\lambda/\beta \cos \theta

where $\theta$ is the Bragg angle, $\lambda$ is the wavelength of the X-rays, $d$ is the mean dimension of the crystallite size composing the powder sample, $\beta$ is the full width at half maximum of the pure diffraction profile on the 20 scale in radians and $k$ is a constant. In the determination of particle size by this method, it must be realized that instrumental effects might also increase the width of reflection and correction for instrumental broadening must be applied. This method can be used for the determination of approximate size of small crystals.

2.2 TGA-DTA

Thermal analysis is defined as a technique in which a physical property is recorded as a function of temperature. Thermo Gravimetric Analysis (TGA) is a technique where the change in mass of a sample is monitored under programmed heating. TGA measures the mass change (loss or gain) of a material with temperature. In Differential thermal analysis (DTA), the heat changes within a material are monitored by measuring the difference in temperature between the sample and a reference material, both of which are heated under identical conditions. These measurements provide qualitative and quantitative information about changes that involve endothermic (heat absorbed) and exothermic (heat evolved) processes via chemical reactions during the heating process. Generally speaking, phase transitions, dehydration, reduction and some decomposition reactions produce endothermic effects whereas crystallization, oxidation and some decomposition reactions produce exothermic effects. TGA/DTA measurements were carried out in the present investigation to study the decomposition pattern, thermal stabilities and phase transition temperature [3].
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In the present study, TGA/DTA analysis was carried out by Mettler Toledo TGA/DSC 1 at a heating rate of 10 ºC/min from 100 to 800 ºC in inert gas (N₂) atmosphere.

2.3 Fourier Transform Infrared (FT-IR) and Raman Spectroscopy

Raman and infrared spectroscopy are two complementary spectroscopic techniques employed to detect vibrations in molecules or semiconductors [4, 5]. A schematic of the different absorption and scattering processes are shown in figure 2.1. In FT-IR, infrared frequency of radiation energy is directed onto the sample. The loss of this frequency of radiation from the beam after it passes through the sample is then detected. Absorption occurs where the frequency of the incident radiation matches with the vibrational frequency of a molecule and the molecule is promoted to a vibrational excited state. They are widely used to get information on chemical structures and physical forms, and provide characteristic spectral patterns (‘fingerprinting’) of the molecule.

![Diagram of IR absorption and Raman scattering processes.]

Figure 2.1 Schematic representations of IR absorption and Raman scattering processes.
In the present study, the IR spectra were measured from 400–4000 cm$^{-1}$ with JASCO FT/IR-5300 model operating at a resolution of 4 cm$^{-1}$, for which the samples were admixed with KBr from Sigma-Aldrich and palletized.

Raman scattering is a nondestructive technique and does not require any special sample preparation techniques like KBr pellet method for IR studies. In the present work HR 800 Horiba Jobin Yvon confocal micro-Raman spectrometer equipped with grating having 1800 groves/mm was used to investigate the Raman peaks of oxide (Bi$_{12}$SiO$_{20}$, Cu$_2$O) and CdS nanocrystals. Calibration was performed with a silicon wafer by utilizing the first-order phonon band of Si at 520 cm$^{-1}$ before and after recording. The spectrometer consists of three excitation laser sources; He: Ne laser which provides 632nm, Argon ion laser working at 514nm, and diode laser providing 785nm wavelengths. The detecting system is a CCD. A notch filter is used in the HR 800 for the rejection of the exciting line. It is specific for one wavelength and it is changed with excitation wavelength source is changed. A joy stick is provided to position the sample exactly under the illumination spot. The notch filter, in particular, is widely used. It is designed to absorb all light of the frequency of the incident laser light. The notch filter has a huge advantage when used; the spectra can be recorded very close to the excitation wavelength without saturating the detector. This reduces the size of Raman spectrometers and improved their efficiency.

2.4 Electron paramagnetic resonance spectroscopy
Electron paramagnetic spectroscopy (EPR) is also known as electron spin resonance (ESR) or electron magnetic resonance (EMR) and measures the transition frequency between electron spin states. EPR spectroscopy is a technique for studying chemical species that have one or more unpaired
electrons, such as free radicals or inorganic complexes possessing a transition metal ion. EPR is a powerful non-destructive analytical method and deals with the absorption of microwave radiation by an unpaired electron (namely free radicals, odd-electron molecules, transition metal complexes, rare earth ions, etc.) under a strong magnetic field [6,7].

EPR or ESR spectra can be generated by either varying the frequency of electromagnetic radiation incident on a sample while holding the magnetic field constant, or varying the magnetic field and keeping the frequency of electromagnetic radiation constant. Usually, the frequency of electromagnetic radiation is kept fixed and magnetic field is varied in order to obtain an absorption spectrum.

The electromagnet generates static/DC magnetic field when current is passed through it. Radiation source (microwave frequency) is a klystron. Sample is placed in EPR tube with typically 4 mm in diameter. The sample is placed in a resonant cavity which admits microwaves through an iris. The radiation may be incident on the sample continuously (i.e., continuous wave) or pulsed. The cavity is located in the middle of an electromagnet and helps to amplify the weak signals from the sample. The source is modulated and the resulting signal generated goes through a phase sensitive detector and the signal is amplified.

In this dissertation, we have used JEOL Company EPR spectrometer with model JES-FA 200, to investigate impurity (paramagnetic) spices in as synthesized nanopowders. In this model, the microwave unit is X band unit which provides (8.65-9.75) GHz range. Magnetic field strength can be varied from 0-1 tesla.
2.5 Microscopy

Microscopy involves the study of objects that are too small to be examined by the unaided eye. There are many types of microscopes, the most common and first to be invented is the optical microscope which uses light other electrons microscope which uses electron to image the sample [8].

2.5.1 Light Microscopy

Light-optical microscopes daylight or light from a lamp is directed via a lens or mirror through the specimen and into the microscope, which creates a real image on the retina of the eye or within an attached camera. A modern light microscope has a magnification of about 1000X and enables the eye to resolve objects separated by 200 nm. As scientists and inventors toiled to achieve better resolution, they soon realized that the resolving power of the microscope was not only limited by the number and quality of the lenses, but also by the wavelength of the light used for illumination. With visible light it was impossible to resolve points in the object that were closer together than a few hundred nanometers. Using light with a shorter wavelength (blue or ultraviolet) gave a small improvement. Immersing the specimen and the front of the objective lens in a medium with a high refractive index (such as oil) gave another small improvement, but these measures together only brought the resolving power of the microscope to just under 100 nm. This is an optical instrument containing one or more lenses producing an enlarged image of a sample placed in the focal plane.

2.5.2 Electron Microscopes

In the 1920s, it was discovered that accelerated electrons behave in vacuum much like light. They travel in straight lines and have wavelike properties, with a wavelength that is about 100,000 times shorter than that of visible light. Compared to conventional optical microscope, an electron microscope offers
advantages including high magnification, large depth of focus, great resolution and ease of sample preparation and observation. Today, electron microscopes have reached resolutions of better than 0.05 nm, more than 4000 times better than a typical light microscope and 4,000,000 times better than the unaided eye. The theoretical resolution limit of conventional optical imaging methodology (200 to 300 nanometers for visible light) was the primary factor motivating the development of recent higher-resolution scanning probe techniques, such as scanning tunneling microscope (STM), atomic force microscopy (AFM), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The specimen in an electron microscope is usually in a dry state, surrounded by a high vacuum.

Accelerated electrons in an FE-SEM or TEM carry significant amount of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions as the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light, and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples; secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrast in composition of multiphase samples (i.e. for rapid phase discrimination). In order to be observed with a FE-SEM, objects are first made conductive for current. This is done by coating them with an extremely thin layer (1.5 - 3.0 nm) of gold. In this dissertation, we have used Carl ZEISS, FEG, Ultra 55 FE-SEM model and Tecnai 20 G2 Stwin, FEI electron microscope operated at 20 kV using Gatan
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CCD camera to analyze particle morphology, crystallinity and elemental analysis.

**2.6 UV-Visible Absorption Spectroscopy**

If the energy of an incident photon corresponds to the energy gap between the ground state of a molecule and an excited state, the photon may be absorbed and the molecule is promoted to the higher energy excited state. It is this change which is measured in absorption spectroscopy by the detection of the loss of that energy of radiation from the light. UV-Vis spectrophotometer is used to characterize the absorption, transmission, and reflectivity of a variety of technologically important materials.

Samples for UV-Vis spectrophotometers are most often liquids, although the absorbance of gases and even of solids can also be measured. Samples are typically placed in a transparent cell, known as cuvette. Cuvettes are typically rectangular in shape; commonly with an internal width of 1 cm. Sample container used must allow radiation to pass over the spectral region of interest. The most widely applicable cuvettes are made of high quality fused silica or quartz glass because these are transparent throughout the UV, visible and near infrared regions. Glass and plastic cuvettes are also common, although glass and most plastics absorb in the UV, which limits their usefulness to visible wavelengths. In the present thesis we performed UV–Vis absorption studies by using JASCO UV-Vis spectrophotometer.

**2.7 Z-Scan Technique**

The Z-scan technique is used to investigate nonlinear optical properties of materials. The Z-scan technique is a single beam technique, which allows the determination of the real and imaginary parts of the third order nonlinear
susceptibility [9]. This technique is a simple, sensitive, single beam method that uses the principle of spatial beam distortion to measure both the sign and the magnitude of refractive nonlinearities of optical materials. The experiment uses a Gaussian beam from a laser in tight focus geometry to measure the transmittance of a nonlinear medium through a finite aperture in the far field as a function of the sample position Z, from the focal plane. Analysis of the transmitted intensity through the sample as the function of sample position (known as Z-scan curve), gives the real and imaginary parts of the third order susceptibility. In addition to this, the sample transmittance without an aperture is also measured to extract complementary information about the absorptive nonlinearities of the sample.

The sensitivity of the experiment to refractive nonlinearities is entirely due to the aperture. The removal of the aperture will make the Z-scan sensitive to absorptive nonlinearities alone. Thus by doing the Z-scan with and without aperture, both the refractive and absorptive nonlinearities of the sample can be studied. The schematic of an open aperture Z-scan is as shown in figure 2.2. Spatially filtered input beam is focused using a lens. The sample is scanned across the focus using a stepper motor controlled by PC. The transmitted light is then collected using another lens (large area) of f ~ 100 mm and fast photodiode (FND100). Different neutral density filters are used for attenuation to ensure that the photodiode does not get saturated. The photodiode output is fed to a lock-in amplifier or a boxcar averager/gated integrator and is finally recorded. The averaged signal is then sent to an interfaced ADC card and then to a computer.
Z-scan technique has the following advantages

- Simplicity of the experimental scheme.
- As a single-beam technique, it has no difficult alignment other than keeping the beam centered on the aperture.
- It can be used to determine both the magnitude and the sign of $n_2$. The sign is obvious from the shape of the transmittance curve.
- Under rather general conditions that are easily fulfilled, the data analysis is quick and simple, making it a good method for screening new nonlinear materials. Under certain conditions, it is possible to isolate the nonlinear refractive and nonlinear absorptive contributions to the far-field transmittance.
- The technique is also highly sensitive, capable of resolving a phase distortion of $\sim \lambda /300$ in samples of high optical quality.
- Finally, the Z-scan can also be modified to study nonlinearities on different time scales as well as higher order contributions.

Figure 2.2 Schematic of the experimental setup of the Z-scan technique.
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The Z-scan technique has been used extensively to study different materials like semiconductors, nano-crystals, semiconductor-doped glasses, liquid crystals, organic materials, biomaterials etc. To enhance its sensitivity and applicability new extensions have been added. A two color Z-scan is used to perform the studies of non-degenerate optical nonlinearities. A much more sensitive technique, EZ-scan (eclipsed Z-scan), has been developed which utilizes the fact that the wings of a circular Gaussian beam are much more sensitive to the far-field beam distortion. A reflection Z-scan technique was introduced to study the optical nonlinearities of surfaces. Z-scan with top-hat beams, elliptical Gaussian beams have been performed resulting in better sensitivity. The Z-scan technique is used to measure two kinds of nonlinear optical properties. Open aperture Z-scan is used for absorptive nonlinearity and the closed aperture Z-scan is used for sign of the refractive nonlinearity.

2.8 Stokes and anti-Stokes luminescence

Figure 2.3 Experimental setup for Stoke and anti-Stokes luminescence measurements.
The experimental setup for the Stokes and anti-Stokes luminescence measurement is shown in figure 2.3. For Stokes luminescence (down conversion) samples were excited with 6 ns pulse duration third harmonic at 355 nm of the Nd: YAG laser with a repetition rate of 10Hz. For recording the anti-Stokes (Up-conversion) luminescence of solid samples, 100-fs pulses delivered by a Ti: sapphire laser at 798 nm with a repetition rate of 80 kHz was employed for excitation. Excitation power was varied by using a continuously adjustable neutral density filter and keeping a fixed distance between the sample and the focusing lens. Up and down conversion luminescence spectra were collected by Ocean Optics fiber spectrometer connected with a computer.

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