4.1 Introduction

Nowadays, scientists and engineers have an impressive array of powerful and elegant tools for acquiring quantitative and qualitative information about the composition and structure of matter. There are varieties of nano-particles synthesized, which are having numerous applications in science and technology. It is always important to characterize these nano-particles at different angles of interests by different instruments [1]. The present chapter gives a brief review of different experimental characterization techniques, which are used by the present author to characterize the synthesized nano-particles.

4.2 X – Ray Diffraction (XRD) by Powder Method

The powder XRD, which is also known as Debye – Scherer method is a nondestructive technique and recognized as a powerful technique for phase identification, chemical analysis and structural determination of various materials. A powder method, which was devised independently in 1916 by Peter Joseph William Debye and P. Scherrer [2] in Germany and in 1917 by A. W. Hull [3, 4] in United States. The work presented in the thesis, emphasizes on the synthesis of metallic nanoparticles. Their crystalline nature and crystal type could be identified from their XRD patterns. When the diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various inter-planar spacing in the crystal lattice, which is exhibited in Figure 4.1. The positions and the intensities of the peaks are used for identifying the underlying structure of the material.

Figure 4.1 Powder Sample Diffract X-ray Beam in Cones

Figure 4.2 schematic representation of powder method
In 1912-1913, the W. L. Bragg [5, 6] developed the Bragg’s Law and the equation is as follows:

\[ n\lambda = 2d\sin\theta \] 4.1

Where \( n \) denotes the order of diffraction, \( \lambda \) represents the wavelength of monochromatic X-rays, \( d \) is the inter-planar spacing between similar atomic planes in a crystal also called the d-spacing and measured in angstroms and \( \theta \) signifies the Bragg angle (angle between incident X-ray and diffraction plane) measured in degrees. For practical reasons the diffractometer measures an angle twice that of the theta angle. Figure 4.2 gives the schematic representation of powder method.

Common targets used in x-ray tubes include Cu and Mo, which emit 8 keV and 14 keV x-rays with corresponding wavelengths of 1.54 Å and 0.8 Å, respectively [7, 8]. X-rays primarily interact with electrons in atoms. When x-ray photons collide with electrons, some photons from the incident beam will be deflected away from the direction where they original travel. If the wavelength of these scattered x-rays did not change, the process is called elastic scattering in that only momentum has been transferred in the scattering process. These are the x-rays that are measured in diffraction experiments, as the scattered x-rays carry information about the electron distribution in materials. Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern therefore allows us to deduce the distribution of atoms in a material. When certain geometric requirements are met, X-rays scattered from a crystalline solid can constructively interfere, producing a diffracted beam.

Various types of micro and nano crystalline powder, thin films and polycrystalline materials can be characterized by powder XRD, including organic and inorganic materials, drugs, minerals, zeolites, catalysts, metals and ceramics. For most applications, the amount of information which is possible to extract depends on the nature of the sample microstructure (crystallinity, structure imperfections, crystallite size and texture) the complexity of the crystal structure (number of atoms in the asymmetric unit cell and unit cell volume), the quality of the experimental data (instrument performances and counting statistics) [9].

There are many applications of the powder method, which are summarized in table 4.1. The ASTM data cards as well as JCPD/S data files are available for large number of substances for identifications and comparison. Identification of phases can be done by powder technique without solving crystal structure or assigning indices to the reflections. There are numerous computer soft-wares available for powder XRD analysis.

### Table 4.1 Applications of Powder XRD [10]

<table>
<thead>
<tr>
<th>Diffraction Line Parameter</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Position</td>
<td>Unit-cell parameter refinement</td>
</tr>
<tr>
<td></td>
<td>Pattern indexing</td>
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<tr>
<td></td>
<td>Space group determination (2θ / absent reflections)</td>
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<tr>
<td></td>
<td>Anisotropic thermal expansion</td>
</tr>
<tr>
<td></td>
<td>Macro stress: sin2ψ method</td>
</tr>
<tr>
<td></td>
<td>Phase identification (d / I)</td>
</tr>
<tr>
<td>Intensity</td>
<td>Phase abundance</td>
</tr>
<tr>
<td></td>
<td>Reaction kinetics</td>
</tr>
<tr>
<td></td>
<td>Crystal structure analysis (whole pattern)</td>
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<tr>
<td></td>
<td>Rietveld refinement (whole pattern)</td>
</tr>
<tr>
<td></td>
<td>Search/match, phase identification</td>
</tr>
<tr>
<td></td>
<td>Preferred orientation, texture analysis</td>
</tr>
<tr>
<td>Width / Breadth and Shape</td>
<td>Instrumental resolution function</td>
</tr>
<tr>
<td></td>
<td>Microstructure: line profile analysis</td>
</tr>
<tr>
<td></td>
<td>Microstructure (crystallite size, size distribution, lattice distortion, structure mistakes, dislocations, composition gradient)</td>
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<tr>
<td></td>
<td>Crystallite growth kinetics</td>
</tr>
<tr>
<td></td>
<td>Three-dimensional microstructure (whole pattern)</td>
</tr>
<tr>
<td>Non-ambient and dynamic diffraction</td>
<td>In situ diffraction under external constraints reaction kinetics.</td>
</tr>
</tbody>
</table>

However, there are certain limitations of powder XRD, such as limited sensitivity (a phase present in quantities lower than 5% by weight is difficult to
detect), peak overlaps may occur for high angle reflections and for non-isometric crystals the analysis of unit cell parameters and indexing pattern is difficult.

The present author has analyzed crystalline nano-particle samples by powder X-ray analysis using Powder Diffractometer system as shown in figure 4.3. The CuKα radiation was used. The crystal structures were determined by using a computer software Powder-X.

4.3 Electron Microscopy

Electron Microscopes (EM) are scientific instruments that use a beam of highly energetic electrons to examine objects on a very fine scale and valuable tool in biology, medicine and material science. This wide spread use of EM is based on the observation and characterization of materials on a micrometer scale (Scanning Electron Microscopes - SEM)) to nanometer (Transmission Electron Microscopes - TEM) [11].

4.3.1 Scanning Electron Microscope (SEM)

SEM images provide topographical, morphological and compositional information makes them invaluable in a variety of scientific and industrial applications. The first Scanning Electron Microscope (SEM) was developed at the RCA Laboratories in New Jersey. The first commercial model was delivered in 1958 by AEI Company to Pulp and Paper Research Institute of Canada. The basic components involved in working of a SEM are shown in Figure 4.4. A focused beam of electrons from a fine probe is rastered over the surface of the specimen. The scan coils and objective lens allows the horizontal and vertical deflection of electron beam to scan the specimen surface. The interaction of electron beam with the surface leads to expulsion of electrons or photons from the specimen surfaces which are further collected with the help of detectors. Thus the formed image is a representation of the corresponding point where the electron beam strikes the specimen surface. The SEM generally operates on a voltage ranging between 2 to 50 kV and its beam diameter that scans the specimen is 5 nm – 2 μm.

The low energy secondary electron detection gives topographic contrast (surface texture and roughness) and can resolve surface structure up to 100 nm. However, detection of high energy backscattered electrons gives both compositional and topographic information, good atomic number contrast but poor lateral resolution as compared to secondary electron image.

Advantages

- Analysis of conducting material is possible.
- Based on interaction with surface only so no requirement of electron-transparent sample.
- 3D imaging of the specimen is possible.
Disadvantages

- Low resolution, usually above a few tens of nanometers.
- Staining of non-conducting material is required.

4.3.2 Energy Dispersive Analysis of X-rays (EDAX)

Energy dispersive X-ray spectrometer (EDAX or EDS) attached to the SEM analyses characteristic X-ray radiation emitted (characteristic lines $K_{\alpha}$ and $K_{\beta}$) from the specimen when the electron beams interact with the specimen [12]. They are called the characteristic lines to emphasize that the wavelength of them are fixed and characteristic to the emitting element. The phenomena are called the fluorescence. It provides a basis for a method of chemical analysis. The intensities of the peaks can be compared with the peaks of a standard sample to obtain the relative amounts of each atomic species, whereby accurate composition of the sample can be determined. In the present study SEM & EDS of samples analysis Philips XL30 ESEM TMP was used, which is shown in figure 4.5. This setup is available at Dept. of Metallurgical & Material Engineering, M. S. University of Baroda, Baroda.

4.3.3 Transmission Electron Microscopy

The first transmission electron microscope was developed by two German researchers Max Knoll and Ernst Ruska in the year 1931. In TEM, we utilize the electrons that go through a very thin specimen (<200 nm) and detect scattered electrons as a result of strong interaction between electrons and matter. Recording image, diffraction pattern, x-ray spectrum and electron energy loss spectrum gives topographic, compositional and crystallographic information. Figure 4.6 show different components of a TEM. It consists of three types of lenses - condenser, objective, and projector lenses which are involved in the formation of final image. The condenser lens controls the brightness of the beam and confines the electron beam coming from the filament onto the specimen. The objective lens forms the preliminary enlarged image of the illuminated portion of the specimen whereas the projector lens facilitates the further enlargement of illuminated portion. The electrons that are transmitted through the specimen are involved in image formation while the electrons that can’t pass through or get deflected by dense atoms in the specimen are deducted from the image. An aperture in objective lens can be used to eliminate the effect of these scattered electrons on the formed image. Thus, a contrast image is formed. Finally, the enlarged image is projected onto the fluorescent screen or photographic film with the help of projector lens, or a CCD camera for detection. In order to further enhance the magnification, an intermediate lens can be placed between the objective and projector lens [31].

Sample Preparation: The specimen should be very thin, less than 100 nm as TEM allows strong interaction between electrons and matter. The thin specimens can be achieved by mechanical thinning.

TEM’s find application in cancer research, virology, materials science as well as semiconductor research and nanotechnology. Alternate modes of use allow the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging [32]. In the present investigation, PHILIPS (CM-200) TEM setup having resolution up to 2.4 Å and accelerating voltage 20 - 200 kV, available at SAIF center, IIT Bombay and Hitachi (H-7500) model, UCIM, Punjab University was used.

Figure 4.6(a) Internal Mechanism (b) Typical TEM Set – up

Advantages

- It allows determination of structure and phase and identification of defect.
- High resolution (approx 0.2 nm) and magnification (over one million times).
- No requirement of metallic stain coating for sample observation.
- Allows imaging of crystalline lattice.

Disadvantages

- Trained manpower requirements for operation and analysis.
- Expensive capital cost as well as maintenance.
- Does not allow analysis of samples that are not electron transparent.
4.4 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission of a solid, liquid or gas. Vibrational motion of chemical bonds occurs in the infrared region of the energy beam. The Fourier Transform Infrared Spectroscopy exploits this phenomenon. When a sample is exposed to IR energy this energy couples with the energy of the sample. If the impinging IR energy is in resonance with the energy of the chemical bond in the sample the intensity of the beam is measured before and after it interacts with the sample. The incident radiation can be detected in transmission or reflection experiments. The intensity is then plotted as a function of the frequency in the IR spectrum. Thus infrared spectroscopy is a useful technique for characterizing materials and obtaining information on the molecular structure, dynamics and environment of a compound. In an infrared spectrum, the absorption or transmittance peaks correspond to the frequencies of vibrations between the bonds of the atoms making up the material. From the characteristic peaks, different functional groups present in the compound can be identified. This aspect makes infrared spectroscopy quite useful in material characterization.

The basic components of an FTIR are shown schematically in Figure 4.7. The infrared source emits a broad band of different wavelength of infrared radiation. The IR radiation goes through an interferometer that modulates the infrared radiation. The interferometer performs an optical inverse Fourier transform on the entering IR radiation. The modulated IR beam passes through the gas sample where it is absorbed to various extents at different wavelengths by the various molecules present. Finally the intensity of the IR beam is detected by a detector. The detected signal is digitized and Fourier transformed by the computer to get the IR spectrum of the palletized sample.

The present author has used Nicolet 6700 FT-IR spectrometer as shown in figure 4.8 having optical resolution of 0.04 cm⁻¹, in the range from 400 cm⁻¹ to 4000 cm⁻¹ in KBr disc medium. The FTIR set up available at Physics Department of Saurashtra University was used for the analysis.

4.5 Thermal Studies

According to International Confederation for Thermal Analysis and Calorimetry (ICTAC), thermal analysis is defined as a group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. These methods find widespread use for both quality control and research applications of various substances, such as, oxides, polymers, pharmaceuticals, crystals, clays, minerals, metals and alloys.

4.5.1 Thermo Gravimetric Analysis (TGA)

Thermo gravimetric analysis is a technique in which the mass of a substance is measured as a function of temperature or time while the substance is subjected to a controlled temperature program. The curve obtained in a thermo gravimetric analysis is called thermogram (TG), or a thermal spectrum, or a thermal decomposition curve and its first derivative is called a derivative thermogram (DTG).
In TGA the furnace is normally an electrical resistive heater and the temperature range for most of the furnace is from ambient to 1000-2000 °C. The rate of heat exchange between the furnace and the sample depends on the heating rate which influences the TG curve in a number of ways. These thermal spectrums characterize a system in terms of temperature dependence of its thermodynamic properties and physical-chemical kinetics.

The TGA finds applications in the study of thermal degradation, decomposition, dehydration of different samples. The chemical reaction resulting in changes of mass such as absorption, adsorption and desorption can also be studied.

4.5.2 Differential Thermal Analysis (DTA)

DTA is a technique in which the temperature difference between a substance and a reference material is measured as a function of temperature whilst the substance and reference material are subjected to a controlled temperature program [15]. DTA provides information on the chemical reactions, phase transformations, melting, crystallization or a glass transition and structural changes that occur in a sample during a heat-up cycle. The DTA measures the differences in energies released or absorbed, and the changes in heat capacity of materials as a function of temperature. The DTA identifies binder burnout, carbon oxidation, sulfur oxidation, structural clay collapse, Alpha to Beta quartz transition, carbonate decompositions, recrystallizations, melting and cristobalite transitions, melting, solidification or solidus temperature, glass transition temperature (TG), curie point, energy of reaction, heat capacity, and others. The transition enthalpy is estimated from the DTA curve using the heat capacity of the heat sensitive plate as a function of temperature.

4.5.3 Differential Scanning Calorimetry (DSC)

DSC is a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature whilst the substance and reference material are subjected to a controlled temperature program [15]. A DSC analyzer measures the energy changes that occur as a sample is heated, cooled or held isothermally, together with the temperature at which these changes occur. Usually, for the power compensation DSC curve, heat flow rate should be plotted on the ordinate with endothermic reactions upwards, and for the heat-flux DSC curve with endothermic reactions downwards. There are two methods of carrying out DSC, namely, (i) Power compensated DSC, and (ii) Heat-flux DSC. In the present study the heat flux type of DSC was used.

In the present study, the thermal analysis TG, DTA and DSC of the materials were carried out to determine simultaneous changes of mass and caloric reactions using PC controlled Linseis Simultaneous Thermal Analyzer (STA) PT-1600, in the atmosphere of air from 35 °C to 1000 °C at a heating rate of 15 °C/min. TA-WIN and WIN-STA software used for testing and analysis. The set up for thermal analysis is shown in figure 4.9 with measuring head and crucible, which is available at Physics Department of Saurashtra University.

Figure 4.9 (a) Linseis Simultaneous Thermal Analyzer PT-1600, (b) Measuring head and crucible

4.6 Dielectric Studies

Materials, which are electric insulators or in which an electric field can be sustained with a minimum dissipation of power, are known as dielectric materials [16, 17]. Ferrites are very good dielectric materials and hence it is important to study their dielectric behavior at different frequencies. The dielectric properties of ferrites depend on several factors, including the method of preparation. The dielectric constant and loss tangent can be measured by using a LCR meter. It is evident from the name of LCR meter that it is basically inductance ‘L’, capacitance ‘C’ and resistance ‘R’ measuring device.

Dielectric constant (k) or Relative Permittivity (εr)

Dielectric constant is defined as the ratio of the capacitance (C) of a capacitor filled with the given material to the capacitance (C0) of an identical capacitor in a vacuum without the dielectric material. The dielectric constant can also be defined as the ratio of the permittivity of the dielectric material (ε) to the permittivity of vacuum materials.
The dielectric constant is, therefore, also known as the relative permittivity ($\varepsilon_r$) or absolute permittivity of the material and is always greater than 1.

\[
\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}
\]

Where, \( d \) is the thickness of the pellet, \( \varepsilon_0 \) is the vacuum dielectric constant (permittivity of free space, \( \varepsilon_0 = 8.854 \times 10^{-12} \text{ F/m} \)) and \( A \) is the area of the pellet.

**Complex Relative Permittivity ($\varepsilon^*$)**

Permittivity relates to the ability of material to transmit an electric field. The response of materials to alternating fields is characterized by a complex permittivity,

\[
\varepsilon^* = \varepsilon' - j\varepsilon'' = |\varepsilon|e^{-j\delta}
\]

Where \( \varepsilon' \) is the real part of the relative permittivity (i.e. the dielectric constant), which is related to the stored energy within the medium; and \( \varepsilon'' \) is the imaginary part of the relative permittivity, which is related to the dissipation (or loss) of energy within the medium. Equation (4.3) expresses the complex permittivity in two ways, as real and imaginary or as magnitude and phase.

**Dielectric Loss**

The dielectric loss is a measure of the energy absorbed by dielectric. The ratio of imaginary part to the real part of the relative permittivity is known as dielectric loss or the dissipation factor \( D \).

\[
D = \tan\delta = \frac{\varepsilon''}{\varepsilon'}
\]

**A. C. Conductivity and A.C. Resistivity**

The A. C. conductivity is one of the studies done on solids in order to characterize the bulk resistance of the sample. The values of a. c. conductivity and a. c. resistivity were calculated for the different frequencies of the applied electric field using the following formulae,

\[
a.\text{c. conductivity, } \sigma_{ac} = \frac{2\pi f C L}{A}
\]

\[
a.\text{c. resistivity, } \rho_{ac} = \frac{1}{\sigma_{ac}}
\]

where, \( f \) is the frequency, \( C \) is the capacitance, \( D \) is the dissipation factor, \( t \) is the thickness of the pellet and \( A \) is the area of the pellet.

---

**Figure 4.10 LCR Meter**

In the present investigation the dielectric study was carried out by measuring different parameters such as capacitance and dielectric loss of the pressed pellets of samples of known dimension at room temperature on Agilent 4284A Precious LCR Meter using specially designed our home made sample holder with my specially design computer software program for high accuracy and fast measurement, within the frequency range from 50 Hz to 1 MHz. Figure 4.10 shows the photograph of the set up. The powdered samples were pelletized by using a die of 10 mm internal diameter and applying 10 ton pressures.

**4.7 Magnetic Characterizations [Magnetometry]**

The experimental study of magnetic materials requires (a) a means of producing the field which will magnetize the material, and (b) a means of measuring the resulting effect on the material. The magnetic behavior of magnetic materials provides information about spin structure, anisotropy and phase transitions. The aim of magnetometry is to measure the saturation magnetization (either intrinsic or induced by applied field) of a material. The various types of magnetometers fall within two categories:

1. Measuring the force acting on a sample in an inhomogeneous magnetic field: a) Magnetic balance b) Magnetic Pendulum
2. Measuring the magnetic field produced by a sample: (A) Hysteresis loop technique (B) Vibrating Sample Magnetometer (VSM)

**4.7.1 Hysteresis loop technique**

A hysteresis loop shows the relationship between the induced magnetic flux density (B) and the magnetizing force (H). It is often referred to as the B-H loop. An example hysteresis loop is shown below.
The saturation magnetization measurements on the powder samples of the systems Co$_x$Mn$_{1-x}$Fe$_2$O$_4$ and Co$_x$Ni$_{1-x}$Fe$_2$O$_4$ were carried out on an alternating current electromagnet type high field (4 kOe) hysteresis loop tracer at Department of Physics, Saurashtra University, Rajkot. A block diagram of hysteresis loop tracer shown in figure 4.11 [18]. Distortion free hysteresis loops can be obtained only for samples that can develop a pick magnetic moment of 1 emu or more.

4.7.2 Low field AC susceptibility

AC magnetic measurements, in which an AC field is applied to a sample and the resulting AC moment is measured, is time-dependent. AC measurements yield information about magnetization dynamics.

In AC magnetic measurements, a small AC drive magnetic field cause a time-dependent moment in the sample. The field of the time-dependent moment induces a current in the pickup coils, allowing measurement without sample motion. The detection circuitry is configured to detect only in a narrow frequency band, normally at the fundamental frequency. As long as the AC field is small, the induced AC moment is $M_{AC} = (dM/dH) \cdot H_{AC} \sin (\omega t)$ where $H_{AC}$ is the amplitude of the driving field, $\omega$ is the driving frequency and $\chi = dM/dH$ is the slope of the $M$ ($H$) curve, called the susceptibility. The susceptibility is the quantity of interest in AC magnetometry. $\chi$ is called the Mass susceptibility and has unit emu/g Oe in c.g.s. and weber/ampere kg in M. K. S.

Since the AC measurement is sensitive to the slope of $M$ ($H$) and not to the absolute value, small magnetic shift can be detected even when the absolute moment is large. The AC susceptibility is often known as the dynamic susceptibility and measurement yields two quantities: the magnitude of the susceptibility $\chi$, and it's out of phase component. The AC susceptometry, very sensitive to thermodynamic phase changes, is often used to measure transition temperature, which allows one to probe all the interesting magnetic phenomena [19].

The thermal variation of the low field AC susceptibility of these ferrites samples was obtained by using the instruments, which consist of (i) magnetic field unit (ii) magnetization unit and (iii) temperature unit. The magnetic field is produced by a double (Primary and secondary) coil set up i.e. Helmholtz coil, operating at a frequency of 263 Hz with rms field varying between 0 to 10 Oe. The two coils are oppositely wound relative to each other producing uniform magnetic field along the axis perpendicular to the coils. For the magnetization measurement a pick up coils is provided at the centre of a Helmholtz coil.

The temperature variation from RT to 800 K was achieved using a platinum wire wound silica tube, which act as a furnace to heat the sample. The overheating of the coil is avoided by water circulars system as a precaution against the burning or leaking of the coil. The temperature was sensed by platinum-Rhodium thermocouple calibrated against the current in the heating element. Variable current was provided to the heating element by a variable power supply.

The sample tube is held in such a way that the sample material can be located in the middle of the pickup coil. By applying the current to the Helmholtz coil, the change in magnetization of the sample produces EMF in the pickup coil. The signal is then digitized by an analog to digital converter (ADC) and then fed to a digital panel.
magnetometer. The block diagram and the photograph of the susceptibility instrument are shown in the figure 4.12.

**Figure 4.12 Block cum circuit diagram of susceptibility**

### 4.7.3 Vibration Sample Magnetometer (VSM)

Vibration sample magnetometer (VSM) is an instrument commonly employed for characterization of magnetic behaviors. The working principle of VSM is based on the Faraday’s Law of induction, according to which the voltage induced (V) in an electrical circuit is proportional to the rate of change of magnetic flux (φ) linking the circuit [20]. This relation can be demonstrated by the following relationship,

\[ V = -N \frac{\Delta \phi}{\Delta t} \]

where \( N \) is the number of loops in the electrical coil and \( \frac{\Delta \phi}{\Delta t} \) the rate of change of magnetic flux. As magnetic induction \( B = \frac{\phi}{A} \) (A is the cross-sectional area of the coil), the above equation can also be written as

\[ V = -N A B \frac{dB}{dt} \]

Accordingly, the change of magnetic induction can be obtained by measuring the electrical voltage (or current) induced. In VSM, the sample is placed in a constant magnetic field. Vibration of the sample results in the change of magnetic flux through the pick-up coils positioned close to it. A voltage is therefore induced and measured using a lock-in amplifier. This voltage is proportional to the magnetic moment of the sample.

The present author has used VSM make by Lake Shore 7404 (as shown in figure 4.13) available at CIF center, Pondicherry University.

**Figure 4.13 Photograph of lakeshore VSM 7404**

### 4.8 Raman Spectroscopy

Raman spectroscopy is based on the Raman effect, a phenomenon where a change in frequency occurs when light is scattered in a material. In Raman spectrometers, a monochromatic light (laser) shines on and excites molecules in the sample, which subsequently scatter the light. While most of the scattered light is at the same wavelength as that of the source light (Rayleigh scattering), some is scattered at different wavelengths. This results from phonons losing (stokes process) or gaining (anti-stokes process) energy by an inelastic collision of incident light with molecules. The exchange of energy between light and molecules can be described as the following equation [21]:
The energy difference between the monochromatic light and Raman scattered light is called the Raman shift, the intensity of which can be measured and illustrated as a Raman spectrum. As the position and intensity of Raman lines in the Raman spectrum are determined by the nature and environment of the molecule that scatters the light, Raman spectrum can be used to study molecular structures and determine their chemical identities. According to the above equation, Raman lines have two categories: anti-Stokes lines (with frequency of $v_0+v_i$) and Stokes lines (with frequency of $v_0-v_i$). As the population of molecules at ground state is much larger than that at excited state, the Stokes lines are stronger than the anti-Stokes lines under normal conditions. Since both give the same information, it is customary to measure only the stokes side of the spectrum. The basic components of a Raman spectrometer include an excitation laser source, a monochromator or spectrograph, a sample illumination system, a signal processing system consisting of a detector, amplifier and an output device. In this work, Raman spectroscopy was employed for phase characterization, structural analysis and studies of cation distribution. It was carried out using a Renishaw micro-Raman system at backscattering geometry equipped with a liquid nitrogen-cooled CCD detector. A Helium-Neon laser operating at 632.8 nm was employed as the excitation source, which was operated at a power rate of 2.5 and 10 mW. The laser beam was focused onto the samples with a spot size of approximately 1μm.

Experimental Techniques

\[ hv_i = hv_0 \pm \hbar \nu \]

where \( \nu_i \): frequency of the scattered light quanta, \( v_0 \): frequency of the incident light quanta and \( \nu \): frequency of molecular vibration.

4.9 ESR Spectroscopy

The EPR measurements were carried out by Varian make E Line Century X-band EPR spectrometer (Model-E-112). The measurements were done at 9.36 GHz with modulation frequency 100 KHz. DPPH was used as standard reference material for field marker. The samples were taken in spin free quartz capillary tubes. These EPR spectra were analyzed to get the information about spin concentration and spin-spin relaxation.

\( \xi \) Origin of an EPR signal

Every electron has a magnetic moment and spin quantum number \( s = 1/2 \), with magnetic components \( m_s = +1/2 \) and \( m_s = -1/2 \). In the presence of an external magnetic field with strength \( B_0 \), the electron's magnetic moment aligns itself either parallel (\( m_s = +1/2 \)) or anti-parallel (\( m_s = -1/2 \)) to the field, each alignment having a specific energy. The parallel alignment corresponds to the lower energy state, and the separation between it and the upper state is \( \Delta E = g_e \mu_B B_0 \), where \( g_e \) is the electron's so-called Lande g-factor and \( \mu_B \) is the Bohr magneton. This equation implies that the splitting of the energy levels is directly proportional to the magnetic field's strength, as shown in the figure 4.15. An unpaired electron can move between the two energy levels by either absorbing or emitting electromagnetic radiation of energy \( \epsilon = \hbar \omega \) such that the resonance condition, \( \epsilon = \Delta E \), is obeyed. Substituting in \( \epsilon = \hbar \omega \) and is \( \Delta E = g_e \mu_B B_0 \) leads to the fundamental equation. Experimentally, this equation permits a large combination of frequency and magnetic field values, but the great majority of EPR measurements are made with microwaves in the 9000 - 10000 MHz (9 - 10 GHz) region, with fields corresponding to about 3500 G [22]. The energy principle of ESR spectra can be generated by either varying the photon frequency incident on a sample while holding the magnetic field constant, or doing the reverse. In practice, it is usually the frequency which is kept fixed. A collection of paramagnetic centers, such as free radicals, is exposed to microwaves at a fixed frequency.
Figure 4.15 Splitting of energy level

By increasing an external magnetic field, the gap between the $m_s = +1/2$ and $m_s = -1/2$ energy states is widened until it matches the frequency of the microwaves, as represented by the double-arrow in the diagram above. At this point the unpaired electrons can move between their two spin states. Since there typically are more electrons in the lower state, due to the Maxwell-Boltzmann distribution there is a net absorption of energy, and it is this absorption which is monitored and converted into a spectrum.

**Experimental Techniques**

The schematic diagram of an EPR spectrometer is shown in Figure 4.16. The basic features of a spectrometer are:

1. A large electromagnet and its associated power supply
2. Source of microwave radiation—a klystron or a Gunn diode (for X-bands frequency is 9.36GHz)
3. A sample cell (resonant cavity)
4. A detection system
5. A recorded or oscilloscope

Figure 4.16 (a) Block diagram of a typical X-band ESR spectrometer (b) Q- X-band ESR Spectrometer

By increasing an external magnetic field, the gap between the $m_s = +1/2$ and $m_s = -1/2$ energy states is widened until it matches the frequency of the microwaves, as represented by the double-arrow in the diagram above. At this point the unpaired electrons can move between their two spin states. Since there typically are more electrons in the lower state, due to the Maxwell-Boltzmann distribution there is a net absorption of energy, and it is this absorption which is monitored and converted into a spectrum.
In the case of electron spin transitions, this corresponds to radiation in the microwave range. The energy differences between the two spin.

\[
\Delta E = E_+ - E_- = \frac{h}{\beta B}
\]

where \( h \) is Planck’s constant \( (6.626 \times 10^{-34} \text{ Js}) \), \( \beta \) is the frequency of radiation, \( B \) is the Bohr magneton \( (9.274 \times 10^{-24} \text{ J T}^{-1}) \), \( B \) is the strength of the magnetic field in Tesla, and \( g \) is known as the g-factor. The g-factor is a unit less measurement of the intrinsic magnetic moment of the electron, and its value for a free electron is 2.0023. The value of \( g \) can vary, however, and can be calculated by rearrangement of the above equation

\[
g = \frac{h}{\beta B}
\]

using the magnetic field and the frequency of the spectrometer. Since \( h \), \( \beta \), and \( B \) should not change during an experiment, \( g \) values decrease as \( B \) increases. The concept of \( g \) can be roughly equated to that of chemical shift.

### 4.10 Thermography

Thermal images, or thermograms [24], are actually visual displays of the amount of infrared energy emitted, transmitted, and reflected by an object. The image shows the viewer an approximation of the temperature at which the object is operating, the camera is actually using multiple sources of data based on the areas surrounding the object to determine that value rather than detecting the actual temperature. This phenomenon may become clearer upon consideration of the formula Incident Energy = Emitted Energy + Transmitted Energy + Reflected Energy where Incident Energy is the energy profile when viewed through a thermal imaging camera. Emitted Energy is generally what is intended to be measured. Transmitted Energy is the energy that passes through the subject from a remote thermal source. Reflected Energy is the amount of energy that reflects off the surface of the object from a remote thermal source. If the object is radiating at a higher temperature than its surroundings, then power transfer will be taking place and power will be radiating from warm to cold following the principle stated in the Second Law of Thermodynamics. So if there is a cool area in the thermogram, that object will be absorbing the radiation emitted by the warm object. The ability of both objects to emit or absorb this radiation is called emissivity.

In order to perform the role of noncontact temperature recorder, the camera will change the temperature of the object being viewed with its emissivity setting. Other algorithms can be used to affect the measurement, including the transmission ability of the transmitting medium (usually air) and the temperature of that transmitting medium. All these settings will affect the ultimate output for the temperature of the object being viewed.

#### Emissivity

Emissivity is a term representing a material’s ability to emit thermal radiation. Each material has a different emissivity, and it can be difficult to determine the appropriate emissivity for a subject. A material’s emissivity can range from a theoretical 0.00 (completely not-emitting) to an equally theoretical 1.00 (completely emitting); the emissivity often varies with temperature. An example of a substance with low emissivity would be silver, with an emissivity coefficient of 0.02. An example of a substance with high emissivity would be asphalt, with an emissivity coefficient of 0.98. The rate (percentage) of emission of infrared radiation will thus be a fraction of the true contact temperature. This fraction is called emissivity.

To make a temperature measurement of an object, the thermographer will refer to the emissivity table to choose the emissivity value of the object, which is then entered into the camera. The camera’s algorithm will correct the temperature by using the emissivity to calculate a temperature that more closely matches the actual contact temperature of the object.

#### Passive vs. Active thermography

In passive thermography, the features of interest are naturally at a higher or lower temperature than the background. Passive thermography has many applications such as surveillance of people on a scene and medical diagnosis (specifically thermology).

In active thermography, an energy source is required to produce a thermal contrast between the feature of interest and the background. The active approach is necessary in many cases given that the inspected parts are usually in equilibrium with the surroundings.

Thermal imaging cameras convert the energy in the infrared wavelength into a visible light display. All objects above absolute zero emit thermal infrared energy, so thermal cameras can passively see all objects, regardless of ambient light. However, most thermal cameras only see objects warmer than −50°C.
Advantages of thermography

- It shows a visual picture so temperatures over a large area can be compared
- It is capable of catching moving targets in real time
- It is able to find deteriorating, i.e., higher temperature components prior to their failure
- It can be used to measure or observe in areas inaccessible or hazardous for other methods
- It is a non-destructive test method
- It can be used to find defects in shafts, pipes, and other metal or plastic parts
- It can be used to detect objects in dark areas
- It has some medical application, essentially in kinesiotherapy


