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Instrumentation & Methodology
This chapter enlists the instrumentation techniques used for characterizing the ferrite compositions and the principles behind them. In addition this chapter also enlists the materials used, their source of procurement and methods used for the synthesis of ferrite compositions.

2.1. DETAILS OF INSTRUMENTS USED

(i) **FT-IR Spectrophotometer**: The FT-IR spectra of the ferrite compositions were recorded in the range of 4000 – 400 cm\(^{-1}\) in nujol as well as on KBr plates using FT-IR spectrophotometer (NICOLET iS50 FT-IR).

The principle of Infrared (IR) spectroscopy is based on the fact that the bonds in a molecule vibrate at characteristic frequencies. When a molecule is exposed to IR radiations, then it can absorb energy at frequencies which are characteristic to that molecule and the molecule gets excited to higher vibrational state. A frequency will be absorbed when its photon energy coincides with the vibrational energy levels of that molecule. Only those bonds are ‘IR active’, which have dipoles within them. This is because the changes produced in the electric field upon vibration of a bond allow infra red photon to interact with the molecule, resulting in its excitation to higher vibrational states [1].

In conventional dispersive type IR spectrophotometer, monochromatic beam of light is directed at a sample and the extent of absorption of light is measured. This process is repeated for each wavelength. Fourier Transform Infrared (FT-IR) spectroscopy works on a different principle. The FT-IR spectrophotometer collects light of all wavelengths simultaneously. An FT-IR spectrophotometer works on the principle of Fourier Transform, which is a mathematical transformation employed to transform signals between time domain and frequency domain.

The FT-IR spectrophotometer uses **Michelson Interferometer**, which consists of a light source, a beam splitter, two front surface coated mirrors (one fixed mirror and one moving mirror) and detector. The schematic diagram of Michelson Interferometer is shown in Fig. 2.1.
Radiation from the source strikes the beam splitter. The beam splitter transmits half of the radiation striking it and reflects the other half. The transmitted beam falls on the fixed mirror, while the reflected beam is directed at the moving mirror. Both the mirrors reflect the beams to the beam splitter. Again, half of the reflected radiation is transmitted and the other half is reflected, resulting in one beam passing to the detector and other half to the source. The beam reflected to the source is “lost”. Now, two beams reach the reflector, one from the moving mirror and other from the fixed mirror. These two beams have an optical path difference, which is determined by the position of the two mirrors. Since, the beams arise from the same source, these are in phase and therefore, these beams interfere. A sinusoidal signal is detected for a particular frequency; whose maximum corresponds to the constructive interference and the minimum corresponds to the destructive interference. This sinusoidal signal is called interferogram. The interferogram is then translated into a spectrum by the process of conversion through Fourier Transform algorithm.

(ii) Transmission Electron Microscopy (TEM): A Transmission Electron Microscope (TEM) works on the same principle as a light microscope but it uses electrons instead of light. This is because electrons have a wavelength
which is much lower than that of light. The wavelength determines the resolution, \( \rho \), of the microscope, 
\[
\rho = \frac{0.61\lambda}{\sin \alpha}
\]
where \( \lambda \) is the wavelength of the light, and \( \alpha \) the maximum angle between incident and deflected beam [2]. Thus, the use of electrons instead of light increases the resolution of the instrument. The schematic representation of a Transmission Electron Microscope is shown in Fig. 2.2.

![Fig. 2.2: A schematic representation of Transmission Electron Microscope](image_url)

A Transmission Electron Microscope (TEM) constitutes: (1) Illumination source or electron gun; (2) two or three lenses which focus electron beam on the sample; (3) an objective lens to form diffraction in back focal plane and the image of the sample on the image plane; (4) some intermediate lenses to magnify the image or the diffraction pattern on the screen. A magnified black and white image is formed from the interaction that takes place between samples and energetic electrons in the vacuum chamber. A vacuum pump is necessary because collision of electrons with charged molecules of air will deflect the electrons and distort the beam.
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The electron gun comprises of a filament (or cathode), generally a hairpin shaped tungsten wire. The electrons are released by applying an accelerating voltage and a small emission current to the surrounding cathode cap, known as Wehnelt cylinder. A resistor is used to generate potential difference between the filament and cathode cap, which results in collection of electrons inside the cap. These electrons are then attracted towards anode, located just below the gun assembly. The electrons then pass through multiple electromagnetic lenses, which are made of tightly wound wrapping of copper wires. The field produced by these lenses is radially symmetric. The condenser lenses collect the electrons of first crossover image and focus them on the specimen. An objective lens is used to focus the image. Intermediate lenses magnify the image coming from the objective lens, which is then projected by the projector lenses on to the phosphorescent screen and can be photographed or displayed on a digital screen.

The TEM micrographs of ferrite compositions were recorded using a Hitachi (H-7500) Transmission Electron Microscope, operated at a voltage of 120 kV. The instrument has a resolution of 0.36 nm.

(iii) **Powder X-Ray Diffraction:** The phase identification of ferrite compositions was done using Powder X-Ray Diffraction (XRD) technique. This technique is a non destructive technique for characterizing the crystalline samples and is based on the principle that various planes of a crystalline material act as three dimensional diffraction gratings for wavelengths similar to the spacing of planes in crystal lattice. In this, X-rays are generated by a cathode ray tube, which are filtered through crystal monochromators to produce monochromatic X-rays. When these X-rays are allowed to fall on a ferrite composition, then the interaction of these X-rays with the specimen produces constructive interference when Bragg’s law is satisfied: 
\[ n \lambda = 2d \sin \theta \] 
where ‘n’ is an integer, ‘\( \lambda \)’ is the wavelength of X- rays used, ‘d’ is the interplanar spacing and ‘\( \theta \)’ is the angle of incidence of X-rays. Each material has a unique interplanar spacing, from which it can be identified [3].

A schematic diagram representing working of a powder X-Ray Diffractometer instrument is shown in Fig. 2.3.
The instrumentation comprises of an X-ray tube, a sample stage and a detector. An X-ray tube is evacuated and consists of a copper block with a metal target anode and a tungsten filament cathode. A high voltage is applied across the electrodes, which fires electrons at the metal target. The accelerated electrons knock out the core electrons from the metal. The electrons in the outermost orbitals drop down to fill the vacancies created by removal of core electrons. In this process, X-rays are emitted. The wavelength of the X-rays emitted is characteristic of the target material (Cu, Fe, Mo, Cr). The X-rays are directed on the specimen at an angle ‘θ’, while the detector receives the X-rays and records their intensity. The sample and the detector are rotated using a goniometer to record the intensity of X-rays at various 2θ values.

The powder XRD patterns of the ferrite compositions were recorded using Panalytical’s X’Pert Pro spectrophotometer with Cu-Kα radiation (λ = 1.5404 Å) comprising of nickel metal as beta filter. Si powder sample was used as an instrument standard and the instrumental broadening, calculated from the (1 1 1) peak was found to be 0.7 Å.

(iv) Vibrating Sample Magnetometer: Vibrating sample magnetometer (VSM, 155, PAR) is an instrument used to determine the magnetic properties, like saturation magnetization, coercivity and remanence of a material. VSM operates on the principle of Faraday’s law of induction, which states that a
changing magnetic field produces electric field. The electric field is measured in order to gather information on magnetic field.

The sample under study is placed in a constant magnetic field and is surrounded by two sensing coils or pick up coils, as shown in Fig. 2.4. The constant magnetic field aligns the domains of a magnetic material along the field direction. The magnetic dipole moment of the sample creates a magnetic field around the sample. The sample is then vibrated in vertical direction at a fixed frequency and amplitude. As the sample is vibrated, the magnetic flux associated with the vertical movement of the sample induces a voltage in the coils, which is proportional to the magnetization of the sample.

Fig. 2.4: A schematic diagram representation of a Vibrating Sample Magnetometer (VSM).

Electrical Measurements: The d. c. electrical resistivity of the ferrite compositions was measured using two probe method. The experimental set up for the measurement of d. c. electrical resistivity is shown in Fig. 2.5. The instrument consists of a digital picoammeter (SES instruments Pvt. Ltd., Model No. DPM-111), a PID controlled oven (Model No. PID- 200), a high voltage power supply (Model No. EHT-11) and a specially designed sample holder. The sample is molded into a pellet and a silver paint is applied on its both sides to make electrical contact. The pellet is then placed between two electrodes of the sample holder.
The measurements are made in the temperature range of 313 – 423 K (40 – 150 °C) and the temperature is increased in the steps of 10 K. The voltage (V) is set at a fixed value. The variation in current (I) with temperature is noted from digital picoammeter. The resistance (R) is calculated from ohm’s law, $V = IR$. The d.c. resistivity ($\rho$) is calculated from resistance (R) using the relation, $R = \rho \frac{I}{a}$, where $I$ is the thickness of the pellet and $a$ is the area of cross-section of the pellet. The error in measurement of resistivity is approximately 3%.

**(vi) UV–Visible Spectrophotometer:** A UV-Visible spectrophotometer works on the principle that molecules undergo electronic transitions on absorbing energy from ultra violet or visible radiations. The electronic transitions occur between highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) of molecules having pi-electrons or non-bonded electrons. The **absorbance** is measured using Beer-Lambert law, where

$$\text{Absorbance, } A = \log_{10} \frac{I_0}{I} = \epsilon \cdot c \cdot l,$$

where ‘$I_0$’ is the intensity of incident light at a given wavelength, ‘I’ is the intensity of transmitted light, ‘$\epsilon$’ is the absorptivity, ‘c’ is the concentration, while ‘l’ is the path length [4].

A monochromatic light beam is split into two equal intensity beams by a half mirrored device. One beam, called the sample beam, passes through a cuvette containing sample solution. Other beam, called the reference beam, is passed through another cuvette containing only the solvent in which the
sample solution is prepared. The intensities of both the beams transmitted are then measured. The intensity of the sample beam after passing through the cuvette is ‘I’, while that of reference beam is ‘I₀’. From the values of ‘I’ and ‘I₀’, the concentration of the sample in solution can be determined. The schematic representation of a UV-Visible spectrophotometer is shown in Fig. 2.6.

![Fig. 2.6: Schematic representation of a UV-Visible spectrophotometer.](image)

The concentration of dyes during the degradation was monitored by UV-visible spectrophotometer JASCO, V-530.

### 2.2. SYNTHESIS OF NANO-FERRITES

Nano-ferrites can be prepared by several methods like sol-gel auto combustion method [5-9], co precipitation method [10-14], ceramic method [15-17], solid state method [18,19], hydrothermal method [20, 21], etc. Among these, the sol-gel approach has attracted much interest due to its inherent advantages like low processing temperature, good stoichiometric control, homogeneous distribution of reactants and production of ultra-fine particles with narrow size distribution. Further, the sol-gel method does not require any filtration step.

In the present study, the ferrite compositions were synthesized using sol-gel auto-combustion method. A schematic diagram representing sol-gel auto combustion method is shown in Fig. 2.7. In this method, the aqueous solutions of reaction precursors, generally nitrates, are mixed together. An appropriate amount of complexing agent is added. The chelating agents are essential because they can effectively complex metal ions of varying ionic sizes, which help their selective precipitation to maintain compositional homogeneity among the constituents. These can also act as a fuel in combustion reaction, being oxidized by nitrate ions.
chelating ligands should contain carboxylate groups or aliphatic amine groups. Citric acid (containing carboxylate groups), glycine (containing carboxylate and aliphatic amine groups) and hydrazine (containing aliphatic amine groups) have often been used. Citric acid is the most commonly used complexing agent, however, other complexing agents like polyvinyl alcohol, ethylene glycol, glycine etc. have also been reported to be used in ferrite synthesis.

![Diagram](image)

Fig. 2.7: A schematic diagram representing sol-gel auto-combustion method.

Then, the pH value of the solution is adjusted to 5 - 7 by adding ammonia solution. The base catalysts are added to speed up the reaction. The solution is then slowly heated and stirred using a hot plate magnetic stirrer till gels are formed. At a point, the gels are ignited and burnt in a self propagating combustion manner, leading to the formation of ferrites. The ferrites are then annealed in a muffle furnace at various temperatures for 2h.

2.3. REAGENTS AND MATERIALS USED

The list of reagents and materials used along with their source of procurement is given in Table 2.1. All the materials and chemicals used were of A. R. or G. R. Grade.
## Table 2.1: Chemicals used and their source of procurement.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Name of chemical</th>
<th>Chemical Formula</th>
<th>Source of procurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cadmium nitrate</td>
<td>Cd(NO₃)₂.4H₂O</td>
<td>Qualigens fine chemicals</td>
</tr>
<tr>
<td>2</td>
<td>Chromium nitrate</td>
<td>Cr(NO₃)₃.9H₂O</td>
<td>Qualigens fine chemicals</td>
</tr>
<tr>
<td>3</td>
<td>Citric acid</td>
<td>C₆H₈O₇.H₂O</td>
<td>Qualigens fine chemicals</td>
</tr>
<tr>
<td>4</td>
<td>Cobalt nitrate</td>
<td>Co(NO₃)₂.6H₂O</td>
<td>Qualigens fine chemicals</td>
</tr>
<tr>
<td>5</td>
<td>Copper nitrate</td>
<td>Cu(NO₃)₂.3H₂O</td>
<td>s.d. fine-chem limited</td>
</tr>
<tr>
<td>6</td>
<td>Ferric nitrate</td>
<td>Fe(NO₃)₃.9H₂O</td>
<td>s. d. fine-chem limited</td>
</tr>
<tr>
<td>7</td>
<td>Hydrogen peroxide</td>
<td>H₂O₂ (30% w/v)</td>
<td>CDH chemicals</td>
</tr>
<tr>
<td>8</td>
<td>Lanthanum nitrate</td>
<td>La(NO₃)₃.6H₂O</td>
<td>CDH chemicals</td>
</tr>
<tr>
<td>9</td>
<td>Manganous chloride</td>
<td>MnCl₂.4H₂O</td>
<td>s. d. fine-chem limited</td>
</tr>
<tr>
<td>10</td>
<td>Nickel nitrate</td>
<td>Ni(NO₃)₂.6H₂O</td>
<td>CDH chemicals</td>
</tr>
<tr>
<td>11</td>
<td>Potassium permanganate</td>
<td>KMnO₴</td>
<td>CDH chemicals</td>
</tr>
<tr>
<td>12</td>
<td>Sulphuric Acid</td>
<td>H₂SO₄</td>
<td>s. d. fine-chem limited</td>
</tr>
<tr>
<td>13</td>
<td>Zinc nitrate</td>
<td>Zn(NO₃)₂.6H₂O</td>
<td>Qualigens fine chemicals</td>
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</tbody>
</table>
REFERENCES: