Chapter 2

Experimental

This chapter gives a brief insight about the experimental facilities employed in preparation of materials and various characterizations done to study the structural, electrical and magnetic properties of the various ferrite materials prepared. The structural properties were studied by using the x-ray diffraction (XRD) method. The electrical properties were studied at room temperature as well as at high temperature by using the technique of dielectric spectroscopy and impedance spectroscopy. The magnetic properties at room temperature and below room temperature up to 70K by using the Mossbauer spectroscopy, ac susceptibility measurements, dc magnetization (ZFC, FC) and hysteresis measurement.
2.1. Synthesis of Nanomaterials

2.1.1 Sol-gel Method

Synthesis of advanced ceramic as nanoparticles is currently gaining widespread interest in material processing technology [1-5]. Owing to the extremely small dimensions of nanostructure materials, a major portion of the atoms lies at the grain boundaries, which in turn are responsible for superior structural, magnetic, electrical and mechanical properties in these materials compared to their conventional coarse grained counterparts [6-8]. Different chemical processes currently in vogue for the synthesis of nanoparticles include co-precipitation [9, 10], combustion method [11] sol-gel method [12, 13], spray pyrolysis [14], micro-emulsion technique [15] and solid state reaction method followed by mechanical milling [16-22]. Among all these methods, sol-gel process allows good control over the size of the material particles, which in turn decides their structural and transport properties (electrical and magnetic). The advantage of this method includes processing at low temperature, mixing at the molecular level and fabrication of novel materials.

In the present thesis, we have synthesized the nanoparticles of the polycrystalline Al doped Ni_{0.2}Cd_{0.3}Fe_{2.5-x}O_{4} (0.0 ≤ x ≤ 0.5) ferrite. The various steps involved in the sol-gel synthesization process are as:

1. High purity 99.9% ‘AR’ grade nitrates or chlorides in appropriate stoichiometric mixtures dissolved into deionized water with the addition of few drops of ethyl alcohol as organic binder.
2. Gel formation.
3. Drying of the gel.
4. Pelletization.

I. Mixing of Nitrates

Analytical Reagent (AR) grade chemicals of Ni(NO_3)_2.6H_2O, Cd(NO_3)_2.4H_2O, Al(NO_3)_3.9H_2O and Fe(NO_3)_2.9H_2O were mixed together in their stoichiometric ratios and were dissolved in deionized water along with addition of few drops of ethyl alcohol to form the solution.
Nanoparticles Synthesis

Sol-Gel Method

AR GRADE NITRATES IN STOICHIOMETRIC RATIOS

Fe(NO₃)₂ Ni(NO₃)₂ Cd(NO₃)₂ Al(NO₃)₃

Addition of Deionized water

Addition of Ethyl Alcohol

Constant Stirring on Magnetic Stirrer at 75 °C till Gel Formation

Dried at 100 °C

Final Heating at 400 °C

Thoroughly Grinded for Hour

Final Product Formed Nanoparticles of

Ni₀.₂Cd₀.₃Fe₂.₅ₓAlₓO₄

Fig. 2.1: Flow chart for the preparation of Ni₀.₂Cd₀.₃Fe₂.₅ₓAlₓO₄ ferrite nanoparticles.
II. Gel Forma tion

The transparent solution was allowed for gel formation on the magnetic stirrer at 75 °C with constant stirring until the gelation starts and the solution becomes viscous and the transparency of the solution is lost.

III. Drying of Gel

The gel formed was dried at 100 °C for 19 hrs followed by grinding for half an hr. The powder formed was heated for 36 hrs at 400 °C to remove any organic material present. The rate of heating and cooling was maintained same, i.e., 1 °C per minute and was finally ground for half an hr.

IV. Pelletization

This is achieved by using die-press technique in which a die of proper shape was filled with calcinated powder and pressed using hydraulic pressure of 5 ton. In our case, pelletization was carried out using a circular shaped dye of 12 mm diameter. The thickness of the pellets were maintained ~3 to 4 mm. Silver coating was done on opposite faces of the pellet to make it as a parallel plate capacitor with ferrite material as the dielectric medium. Fig. 2.1 shows the flow chart used for the preparation of bulk samples.

2.1.2 Solid-State Reaction Technique

Polycrystalline bulk samples of Cd doped Co_{0.5}Fe_{2.5-x}O_4 ferrite samples were synthesized through sol-gel method while Ti doped Mn_{1+x}Fe_{2-2x}O_4 ferrite samples were synthesized through solid-state reaction technique. The solid state reaction method of bulk preparation, also known as ceramic method, has superiority over other methods such as sol-gel or co-precipitation technique due to easiness of the process involved in the technique. This process involves various steps such as:

1. Mixing the required oxide powders in appropriate stoichiometric proportion,
2. Calcination
3. Pelletization
4. Sintering
(i) Mixing of Powders

For the preparation of Mn$_{1+x}$Fe$_{2-2x}$Ti$_x$O$_4$ samples, the high purity ‘AR’ grade oxides of MnO$_2$, TiO$_2$ and FeO were taken according to their stoichiometric weights. The powders were thoroughly mixed and grinded using a mortar and pestle. The process was performed for several hours in order to mix the powders together properly and to achieve the homogeneity in the mixture. The physical uniformity and the chemical homogeneity of the mixtures are of significant importance especially in case of doped samples.

(ii) Calcination

The decomposition of the mixed powder by heating below its melting point is known as calcination. The intention to adopt calcination procedure is to establish the course of nucleation for the grain growth and to felicitate the decomposition of substituent oxides/carbonates. Mixed powders were kept in alumina crucibles and heated in furnace in ambient environment. The course of calcination entails heating the homogeneously mixed powder to an intermediate high temperature, roughly 1000 °C, lower than the final sintering temperature. For Mn$_{1+x}$Fe$_{2-2x}$Ti$_x$O$_4$ samples, the powder samples were calcinated at 1000 °C. Calcination was repeated 3-4 times with intermediate grinding and calcination was done at higher than the previous step.

(iii) Pelletization

In order to make use of these ceramic materials, the calcinated powders must be brought into the desired shapes before the final sintering process. This is achieved by using die-press technique in which a die of proper shape was filled with calcinated powder and pressed using hydraulic press. In our case, pelletization was carried out in a dye of circular shape of 12mm diameter. The thickness of the pellets were maintained ~2 to 3 mm.
Synthesis Method

Solid-State Reaction Technique

AR Grade Oxides In Stoichiometric Amounts

Mixed Thoroughly and Grinded Using Mortar and Pestle for One Hour

Calcination At 1000 °C For 12 Hours (two times)

Pellets Of Circular Shape Compressed From Dried Powder Using 2% PVC

Final Sintering At 1300°C For 24 Hours

Final Product (Bulk Multiferroic) Samples Of Mn$_{1+x}$Fe$_{2-2x}$Ti$_x$O$_4$

Fig.2.2: Flow chart for the preparation of bulk Mn$_{1+x}$Fe$_{2-2x}$Ti$_x$O$_4$ ferrite samples.
(iv) Sintering

After pelletization of calcinated powder, pellets were calcinated at relatively higher temperature and for longer duration than used during calcination. This has been followed by slow cooling with a suitable predefined rate, which is an essential and important process as it favours the required oxygen content in the material. For Mn$_{1+x}$Fe$_{2-x}$Ti$_x$O$_4$ bulk pellets, the final sintering temperature was kept at 1300 °C for 24 hrs followed by slow cooling rate of 5 °C/minute. Fig. 2.2 shows the flow chart used for the preparation of bulk samples.

2.2 Characterization Techniques

2.2.1 X-ray Diffraction

The German Physicist, Von Laue in 1912 was the first who took up the problem of X-ray diffraction (XRD) with the reason that, “if crystals were composed of regularly spaced atoms which might act as scattering centers for x-rays, and if X-rays were electromagnetic waves of wavelength about equal to the interatomic distances in crystals, then it should be possible to diffract X-rays by means of crystals” [23]. Today, X-ray diffraction [24] is a routine technique for the characterization of the materials. A rich variety of information can be extracted from the XRD. This is an appropriate technique for all forms of samples, i.e. powder and bulk as well as thin film. Using this technique, one can get the information regarding the crystalline nature of a material, nature of the phase present, lattice parameter and grain size [25]. From the position and shape of the lines, one can obtain information regarding the unit cell parameters and microstructural parameters (grain size, microstrain, etc), respectively. In case of thin films, the change in lattice parameter with respect to the bulk gives the idea about the nature of strain present in the system.

The interaction of X-ray radiation with crystalline sample is governed by Bragg’s law, which depicts a relationship between the diffraction angles (Bragg angle), X-ray wavelength, and interplanar spacing of the crystal plane. According to the Bragg, the X-ray diffraction can be visualized as X-rays reflecting from a series of crystallographic planes as shown in Figure 2.3. The path differences introduced between a pair of waves
travelled through the neighboring crystallographic planes are determined by the interplanar spacing. If the total path difference is equal to $n\lambda$ ($n$ being an integer), the constructive interference will occur and a group of diffraction peaks can be observed, which give rise to X-ray patterns. The quantitative account of Bragg's law can be expressed as:

$$2d_{hkl}\sin \theta = n\lambda \quad \text{----- (2.1)}$$

where $d$ is the interplanar spacing for a given set of $hkl$ and $\theta$ the Bragg angle.

The intensity of powder diffraction peaks is in principal determined by the structural factor, $F_{hkl}$ as expressed in equation (2.2), which depends on the crystal structures including relative positions of atoms in the unit cell, types of unit cells and other characteristics such as thermal motion and population parameters.

$$F_{hkl} = \sum_{i=1}^{n} g^{i} t^{i}(s) f^{i}(s) \exp \left[ 2\pi i ((hx^{i} + ky^{i} + lz^{i}) \right] \quad \text{----- (2.2)}$$

where $f^{i}(s)$ is the atomic scattering factor, $g^{i}$ is the population factor of $i^{th}$ atom, $t^{i}(s)$ is the temperature factor, $hkl$ are the Miller indices, and $xyz$ are the fractional coordinates of $i^{th}$ atom in the unit cell.

![Fig. 2.3: Geometrical illustrations of crystal planes and Bragg's law.](image)

Bragg's Law: $n\lambda = 2d_{hkl}\sin \theta$
In addition to the primary structural factors, the intensity of diffraction is dependent on other factors, which are not only relevant to sample effects such as its shape and size, grain size distribution, etc., but also on the instruments including detector, slit and/or monochromatic geometry.

For all X-ray diffraction experiments presented in this thesis, a Bruker D8 Advance X-ray diffractometer with Cu Kα (λ = 1.54187Å) radiation was employed (shown in Fig.2.4) and operated at an applied voltage of 30kV and filament current of 40mA. The operating voltage and filament current were increased to 40kV and 50mA respectively in case of nano samples to reduce the background and to ensure single phase nature of the samples. The spinel phase identification for all the samples reported in this thesis were performed by matching the peak positions and intensities in XRD patterns to those patterns in the JCPDS (Joint Committee on Powder Diffraction Standards) database [26].

The diffraction method is based on the effect of broadening of diffraction reflections associated with the size of the particles (crystallites). All types of defects cause
displacement of the atoms from the lattice sites. M.A. Krivoglaz in 1969 [27] derived an equation for the intensity of the Bragg reflections from a crystal defect, which enabled all the defects to be derived conventionally into two groups. The defects in the first group only lower the intensity of the diffraction reflections but do not cause the reflection broadening. The broadening of the reflections is caused by the defects of second group. These defects are micro-deformations, inhomogeneity (non-uniform composition of the substance over their volume) and the small particle size. The size of nanomaterials can be derived from the peak broadening and can be calculated by using the Scherrer equation (2.3), provided that the nanocrystalline size is less than 100nm.

\[ t = \frac{K \lambda}{(\bar{L})_{\text{vol}} \cos \theta} \]  

where \( t \) is the average crystalline dimension perpendicular to the reflecting phases, \( \lambda \) the X-ray wavelength, \( K \) the Scherrer constant which equals 0.9 for spherical particles, whose value depends on the shape of the particle (crystallite, domain) and on diffraction reflection indices (hkl), and \( (\bar{L})_{\text{vol}} \) the volume-weighted average column length, i.e., the number of reflecting planes times their effective distance ‘d’. For spherical particle \( (\bar{L})_{\text{vol}} \) equals 0.75(D)_{\text{vol}}, where D is the grain diameter. The Scherrer formula is quite satisfactory for small grains (large broadening) in the absence of significant microstrain. A microstrain describes the relative mean square deviation of the lattice spacing from its mean value. Based on the grain size dependence of the strain it is reasonable to assume that there is a radial strain gradient, but from X-ray diffraction only a homogeneous, volume-averaged value is obtained.

2.2.2 Field Emission Transmission Electron Microscopy (FETEM)

Transmission Electron Microscopy (TEM) has become a versatile and indispensable tool in exploration of nanomaterials. The complementary imaging, diffraction and spatial resolution microanalysis techniques in TEM provides the information about crystal structure, electronic and/or magnetic structure, size and shape of nanomaterials. The transmitted electrons are also used to visualize the internal crystal structure by bright and dark field imaging and orientation and identification of crystals in selected area electron diffractions. The elemental and chemical information can be simultaneously derived from the analysis of the characteristic X-ray radiations [28-31]. We have used Field Emission
Transmission Electron Microscope (FETEM), model Tecnai 20 G2, for the analysis of our nanoparticles of Al doped Ni$_{0.2}$Cd$_{0.3}$Fe$_{2.5-x}$O$_4$ ferrites, operated at 200 kV. The schematic diagram of the FE-TEM instrument used is presented in Fig.2.5.

### 2.2.3 Field Emission Scanning Electron Microscopy (FE-SEM)

Fig. 2.6 presents the schematic diagram of the Field Emission Scanning Electron microscope (FE-SEM) used for probing surfaces and microstructural characterization of the solid samples [32]. This technique is widely used to get information about the topographical features, morphology, phase distribution, crystal structure, crystal orientation, the presence and location of defects. In FE-SEM, as name suggests, the electron beams are moved by the electric field to scan the sample. In this technique, a beam of electrons is produced by heating a metallic filament. The electron beams, focused with the help of electromagnetic lenses, falls on the sample with energy typically ~30 keV. When the beam strikes on the surface of the sample, backscattered electrons, secondary
electrons, Auger electrons and photons are ejected from the sample with typical energy. Detectors collect the secondary or backscattered electrons and an image is produced on a cathode ray tube screen by recording the intensity of the detected signal as a function of position. The signal magnitude varies as a result of difference in surface topography as the electron beam is scanned across the sample surface. In this way, SEM can be employed to visualize surface features with a good resolution of the order of nanometers. In the present thesis work, we used Field Emission Scanning Electron Microscope MIRA II LMH, H.S. Code: 9012.10.1000 for the characterization of our samples.

2.2.4 Energy Dispersive X-ray Spectroscopy (EDX)

EDX is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of XRF. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure, allowing X-rays that are characteristic of an element's atomic structure, to be identified uniquely from each other. Fig. 2.7 presents the schematic diagram of EDX set up in connection with FE-SEM used
for the characterization of our samples. There are four primary components of the EDX set up: the beam source; the X-ray detector; the pulse processor; and the analyzer. A number of free-standing EDX systems exist. However, EDX systems are most commonly found on scanning electron microscopes (SEM-EDX) and electron microprobes. Scanning electron microscopes are equipped with a cathode and magnetic lenses to create and focus a beam of electrons and since 1960’s they have been equipped with elemental analysis capabilities. A detector is used to convert X-ray energy into voltage signals; this information is sent to a pulse processor, which measures the signals and passes them onto an analyzer for data display and analysis.

2.2.5 Electrical Properties

In the present work, the dielectric, ac conductivity and impedance measurements have been carried as a function of composition, frequency (42Hz-5MHz) and temperature (300K-473K) using HIOKI-36532-50 HITESTER LCR meter. The temperature was
controlled with accuracy of ±50 mK using Lakeshore (Model 340) temperature controller.

2.2.5.1 Dielectric Measurement

For dielectric and ac impedance measurements, the silver coating was done on the opposite faces of the pellet to make parallel plate capacitor geometry and ferrite material as the dielectric material. The value of dielectric constant ($\varepsilon$) has been calculated using the formula [33]:

$$\varepsilon' = \frac{C_p x}{\varepsilon_0 A}$$ ---- (2.4)

where $\varepsilon_0 = 8.854 \times 10^{-12} \text{ F/m}$, known as permittivity of free space, $x$ is the thickness of pellets, $A$ is the area of cross section of the pellet and $C_p$ is capacitance of the pellet. The complex dielectric constant has been calculated from the relation:

$$\varepsilon'' = \varepsilon' \tan\delta$$ ---- (2.5)

where $\varepsilon''$ is the complex part of the dielectric constant and $\tan\delta$ the dielectric loss.

2.2.5.2 Dielectric Loss ($\tan\delta$)

The energy loss is usually characterized by the dielectric loss factor ($\tan\delta$) which is expressed as the ratio of the imaginary part of the dielectric constant to the real part, i.e.

$$\tan\delta = \frac{1}{2\pi f \varepsilon_0 \varepsilon'' \rho}$$ ---- (2.6)

where $f$ is the frequency of the applied ac field and $\rho$ the resistivity of the dielectric material. The dielectric loss arises when the polarization lags behind the applied field and is caused by the impurities and imperfections in the crystal lattice. The density of a material also plays an important role in the variation of dielectric constant. High porosity and low density results in low dielectric constant and dielectric losses [34].
2.2.5.3 Ac Conductivity

The total conductivity of any system is sum of the ac conductivity and dc conductivity and is given by the relationship:

\[ \sigma_{\text{tot}} = \sigma_0(T) + \sigma(\omega, T) \]  \hspace{1cm} (2.7)

The first term at R.H.S. of eq. (2.7) is dc conductivity due to the band conduction, which is a frequency independent function while the second term of the equation represents the pure ac conductivity due to electron hoping between the two Fe ions at octahedral sites. In the present study of nano as well as bulk ferrite materials, we have studied the ac conductivity as a function of frequency and temperature for different compositions using the relation [35]:

\[ \sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan \delta \]  \hspace{1cm} (2.8)

where \( \omega \) is angular frequency.

2.2.5.4 Impedance Spectroscopy

Bauerle [36-38], was the first to use this technique in 1969 to separate bulk from interfacial properties in polycrystalline ceramics. In complex impedance diagrams (Nyquist or Cole-Cole plot) the imaginary part of the impedance \( Z'(\omega) \) is plotted against the real part of impedance \( Z''(\omega) \). The response of an ideal parallel circuit of resistance \( R \) and capacitance \( C \) is a semicircle centered on the real axis. \( R \) is determined from the diameter of the semicircle, whereas \( C \) is calculated from the frequency of semicircle maximum.

Impedance spectroscopy is ideal for investigating the electrical response of dielectric materials as a function of frequency. It is a powerful technique for unraveling the complexities of materials, whose properties and applications depend on the close control of structure, composition, ceramic texture, dopants (or defects) and dopant distribution, which functions by utilizing the different frequency dependences of constituent components for their separation. The impedance analysis of a material is based on an idealized circuit model with discrete electrical components. The analysis is
mainly accomplished by fitting the impedance data to an equivalent circuit, which is representative of the material under investigation. It has been among the most useful investigation techniques since the impedance of grains can be separated from the other sources of impedance, namely grain boundaries and electrode effects [39]. When the grain boundary resistance is larger than the resistance of bulk, two semicircles are often obtained in Cole-Cole plot. Deviations from ideal semicircles have been attributed to the distribution of relaxation times arising from the micro-structural inhomogeneity or disorder in the samples [40, 41].

![Diagram of LCR meter setup](image)

**Fig. 2.8:** Schematic diagram of the LCR meter setup.

A sine wave signal was fed to the input terminal (T1) of the LCR meter and the sample from the signal generator (SG) terminal. The output (T0) measured the output signal from the sample, which was voltage drop across a standard resistance of 1kΩ. Fig. 2.8 shows the schematic diagram of the LCR meter. LCR then automatically analyzed the signals from T1 and T0 to give phase difference (θ) between the input and out signals, i.e., $Z'$ and $Z''$. The complex impedance plot is obtained after plotting $Z''$ versus $Z'$. When an ac voltage $V = V_0 e^{j\omega t}$ is applied across the sample, the current that flows across the sample is given by:
The complex impedance plot can be represented in terms of any of the five possible complex formalisms, the permittivity ($\varepsilon^*$), the admittance ($Y^*$), the electric modulus ($M^*$), the impedance ($Z^*$) and the loss tangent (tan$\delta$). These parameters are related with each other \[42-44\] by the formula:

\[ \tan\delta = \frac{\varepsilon'}{\varepsilon''} = \frac{M'}{M''} = \frac{Y'}{Y''} = \frac{Z'}{Z''} \]  \hspace{1cm} (2.10)

Whereas the real and imaginary parts of the complex impedance are given by:

\[ Z' = \frac{R_g}{1 + \omega^2 C_g R_g^2} + \frac{R_{gb}}{1 + \omega^2 C_{gb} R_{gb}^2} \]  \hspace{1cm} (2.11)

and

\[ Z'' = \frac{-R_g^2 \omega C_g}{1 + \omega^2 C_g R_g^2} + \frac{-R_{gb}^2 \omega C_{gb}}{1 + \omega^2 C_{gb} R_{gb}^2} \]  \hspace{1cm} (2.12)

where the terms $R_g$ and $C_g$ represents the resistance and capacitance of the grain, while $R_{gb}$ and $C_{gb}$ represents the corresponding terms for the grain boundary volume \[45, 46\]. The resistance value for the grain and grain boundary have been calculated from the intercepts on the real part of $Z$ ($Z'$) axis, where as the capacitance values have been calculated from the frequency peaks of the semicircle arcs. Since the value of $Z' = -Z''$ at the maximum, we have;

\[ C_g = \frac{1}{R_g \omega_g} \]  \hspace{1cm} (2.13)

\[ C_{gb} = \frac{1}{R_{gb} \omega_{gb}} \]  \hspace{1cm} (2.14)

Also, the relaxation times $\tau_g$ and $\tau_{gb}$ have been calculated from the frequency peaks.
using the equations:

\[ \tau_g = \frac{1}{\omega_g} = C_g R_g \]  \hspace{1cm} (2.15)

\[ \tau_{gb} = \frac{1}{\omega_{gb}} = C_{gb} R_{gb} \]  \hspace{1cm} (2.16)

2.2.6 Magnetic Properties

2.2.6.1 Mössbauer Spectroscopy

Mössbauer spectroscopy is used to obtain information about the local environment of the Mössbauer nuclei. In contrast to XRD, it also provides information about the materials which do not exhibit long range order (poorly crystalline or amorphous material). This technique is based on the Mössbauer Effect, i.e. the phenomenon of recoil free emission of gamma rays from the nuclei in a solid and its resonance absorption by identical nuclei in another solid. For the Mössbauer spectroscopy measurements presented in this work, we used absorption and emission of the \( \gamma \)-ray energy from the first excited state (3/2) of the stable isotope \( ^{57}\text{Fe} \). In case of \( ^{57}\text{Fe} \) spectroscopy the recoil less 14.4keV gamma rays are emitted by an excited \( ^{57}\text{Fe} \) nucleus obtained from the decay of its parent \( ^{57}\text{Co} \) (half life = 270 days). The source contains parent nucleus of the Mössbauer isotope, embedded in a rigid solid matrix (Rh) to ensure a high recoil free factor \([47, 48]\). The gamma rays emitted from the source are passed through the material (absorber) which is being investigated and rays transmitted through the absorber are detected and counted. If the nuclei in the source and absorber are exact in the same environment, the gamma rays will be resonantly absorbed and an absorption peak will be observed. In order to probe the energy levels of nuclei in different environments, we must scan the energy of the gamma rays which is achieved by moving the source relative to observer. The Doppler Effect produces an energy shift in the gamma ray energy by allowing matching of resonant energy levels in the absorber. One of the simplest cases is shown in Fig. 2.9 and the spectrum recorded is a plot of the transmission intensity versus source velocity in mm/s.

2.2.6.1.1 Hyperfine Interactions

The interaction between a nucleus and its surrounding environment is called hyperfine interaction. In general, these interactions are very small compared to the energy
levels of the nucleus itself, but the extreme energy resolution of the Mossbauer Effect enables these interactions to be observed. The hyperfine interactions may shift energy levels or lift their degeneracy and hence will affect the shape of the Mossbauer spectrum.

### 2.2.6.1.2 Isomer Shift (IS)

The term Isomer shift (IS) arises due to the non-zero volume of the nucleus and the electron charge density due to s-electrons within it leading to an electric monopole interaction, which modifies the nuclear energy levels. The volume of the nucleus in its ground state and the excited states are different and the s-electrons are affected by the chemical environments. The relation between the s-electron density and the nuclear radius is given by:

\[
I.S. = \frac{2}{5} \pi Z e^2 (R_{ex}^2 - R_{gd}^2) [ |\psi_a(0)|^2 - |\psi_s(0)|^2 ]
\]  

(2.17)

where \( R_{ex} \) and \( R_{gd} \) are the nuclear radii of the excited and ground state respectively, \(-e|\psi_a(0)|^2\) and \(-e|\psi_s(0)|^2\), represent the s-electron densities of the absorber and source respectively and \( Z e \) the charge on the resonant nucleus. Any difference in the s-electrons environment between the sources and absorber thus produces a shift in the resonance energy of the transition called isomer shift (see Fig. 2.10 shows the isomer shift in \(^{57}\)Fe Mossbauer transition) which could not be measured directly and so a suitable reference is necessary. In this work, all the results presented the isomer shifts are given.

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**Fig. 2.9:** Mossbauer spectrum showing the simplest case of emitter and absorber nuclei in the same environment.
relative to α-Fe at room temperature. In fact, isomer shift is highly sensitive to the s-electron density, the changes in isomer shift values to different chemical environments in absorbers can give valuable information about the degree of covalency and ionic valance state of Mössbauer isotopes, distinction between high and low spin states.

2.2.6.1.3 Electric Quadrupole Splitting

It is assumed that the nuclear charge distribution is spherical. However, a nucleus that has a spin quantum number \( I > \frac{1}{2} \) has a non-spherical charge distribution. An asymmetric charge distribution around the nucleus causes an asymmetric electric field at the nucleus characterized by a tensor quantity called electric field gradient (EFG). Therefore, the interactions of the nuclear quadrupole moment with the electric field gradient (EFG) at the site of the nucleus give rise to quadrupole splitting (QS) (see Fig. 2.10). The electric field gradient can arise due to the atomic electrons as well as ions, which surround the atoms. In case of \(^{57}\text{Fe}\), the excited state has a spin \( I = 3/2 \) and in the presence of a non-zero electric field gradient, this splits into two sub-levels characterized by \( m_I = \pm \frac{3}{2} \) and \( \pm 3/2 \). This leads to a two line spectrum separated by the quadrupole splitting. Figure 2.10 shows quadrupole splitting for the Mössbauer transition in \(^{57}\text{Fe}\).

2.2.6.1.4 Magnetic Hyperfine Interaction

A splitting in the Mossbauer spectrum arises due to the coupling between the nuclear magnetic moment and the magnetic field at the nucleus is called magnetic hyperfine interaction or Zeeman splitting (see Fig. 2.10). In general, the effective magnetic field experienced by the nucleus is a combination of fields from the atom itself, from the lattice through crystal field effects and from external applied field. This can be considered for now as a single field \( H \), whose direction specifies the principal z-axis. The Hamiltonian for the interaction is given as:

\[
H_m = - \mu \cdot H = g \mu_n I \cdot H
\]  \( \text{---- (2.18)} \)

where \( \mu_n \) is the nuclear Bohr magneton, \( \mu \) the nuclear magnetic moment, \( I \) the nuclear spin and \( g \) the gyromagnetic ratio. The eigen values of Hamiltonian \( E_m \) are given by:

\[
E_m = -g \mu_n H m_I
\]  \( \text{---- (2.19)} \)
Fig. 2.10: *Isomer shift, quadrupole splitting and magnetic hyperfine splitting for the Mössbauer transition in $^{57}\text{Fe}$.*

where $m_\text{I} = +1, -1, -2, \ldots \ldots \ldots -I$ is the magnetic quantum number representing the $Z$-component of $I$. Thus the magnetic field splits the nuclear energy levels of spin $I$ into $(2I+1)$ equally spaced non-degenerate sub-levels. In case of $^{57}\text{Fe}$, the hyperfine splitting for $I = 3/2$ and $1/2$ levels are shown in Fig. 2.10. In ferromagnetic iron metal, the magnetic field at $^{57}\text{Fe}$ nucleus, the magnetic hyperfine field is 33 kOe at room temperature. Therefore, the hyperfine parameters; isomer shift, quadrupole splitting and magnetic hyperfine field can be extracted from the experimental spectra, taking into the account the emission spectra of the source. By comparing with the tabulated data, the environment of the absorbing atom can be determined. However, nuclei in the sample have different surrounding leading to a complicated spectrum which has to be decomposed. The spectrums presented in this work were analyzed using NORMOS (Site/Dist) a computer program developed by R. A. Brand [49].
2.2.6.2 Vibrating Sample Magnetometer (VSM)

A popular method for determining the magnetic properties of wide variety of magnetic samples is Vibrating Sample Magnetometer (VSM). With this technique, the magnetic moment of a sample can be measured with high accuracy. An illustration of VSM is shown in Fig. 2.11. The VSM is based upon Faraday's law, according to which an e.m.f. is induced in a conductor by a time-varying magnetic flux. In VSM, a material is subjected to a uniform magnetic field and is made to undergo mechanical vibrations in the vicinity of pick-up coil, which causes the change in magnetic flux. This induces a voltage in the pick-up coils, which is proportional to the magnetic moment of the sample. In the present study we have used the VSM for the magnetization measurement of nanoparticles of Ni_{0.2}Cd_{0.3}Fe_{2.5-x}Al_{x}O_{4} and Mn_{1+x}Fe_{2.2x}Ti_{x}O_{4} bulk samples from 20 K to the room temperature.

![An illustration of Vibrating Sample Magnetometer](image_url)

Fig. 2.11: An illustration of Vibrating Sample Magnetometer
2.3.1 Fourier Transformation Inferred Spectroscopy

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gases. The term Fourier Transform Inferred Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data are collected and converted from an interference pattern to a spectrum. Today's FTIR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments. FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint", while organic compounds have very rich, detailed spectra; inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds.

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it to absorb light energy. For any given transition between two states, the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state ($E_0$) and the first excited state ($E_1$)]. The energy corresponding to these transitions (between molecular vibrational states) is generally 1-10 kcal/mol which corresponds to the infrared portion of the electromagnetic spectrum [50-52].

\[
E_f - E_i = \frac{hc}{\lambda}
\]

---- (2.20)
where the symbols $E_f$, $E_i$, $h$, $c$ and $\lambda$ represent the excited state energy, ground state energy, plank's constant, velocity of light and wavelength of the infra red light. In the present thesis work, we have used Fourier Transform Infrared Spectrophotometer Nicolet Impact 410 DSP.

2.3.2 Sample Preparation

Solid samples can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. KBr is also transparent in the IR. Alternatively, solid samples can be dissolved in a solvent such as methylene chloride, and the solution placed onto a single salt plate. The solvent is then evaporated off, leaving a thin film of the original material on the plate. This is called a cast film, and is frequently used for the identification. In our case of measurement, we milled our material Ni$_{0.2}$Co$_{0.3}$Fe$_{2.5-x}$Al$_x$O$_4$ nanoparticles with KBr and ground in a mortar and pestle for 10 minutes. The powder material was then pressed into disk shaped thin pellet, which was then analyzed. We used FTIR spectrometer Nicolet Impact 410 DSP model for our measurements.
References

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