CHAPTER 2
Sample preparation and characterization techniques

2.1 Introduction

This chapter describes the sample preparation and experimental techniques, such as: x-ray diffraction (XRD), scanning electron microscope (SEM), vibrating sample magnetometer (VSM) and broadband dielectric spectrometer (BDS), employed to study the structural, electrical, dielectric and magnetic properties of the materials.

2.2 Sample preparation techniques

The following methods are used in this thesis work to synthesize magnetic materials.

i. Solid state reaction

ii. Sol-gel technique

iii. Mechanical milling

iv. Mechanical alloying

2.2.1 Solid state reaction method

In this technique, raw materials (oxides, carbonates, nitrates or hydroxides) of micron size particles are used to synthesize the new compound [1, 2]. The raw materials are mixed in stoichiometric ratio and the ground to make better homogeneity. The mixture, either in pellet form or powder form, is heated at high temperatures (~1000-1500 °C) for typical time more than 6 hours. The heated material is cooled to room temperature and ground once again, and again heated at higher temperature. This process is repeated 2-3 times depending on the nature of material. The heating and cooling process is controlled in precise manner (5-10 °C/min).

For example, (1) formation of spinel ZnCr$_2$O$_4$ using ZnO and Cr$_2$O$_3$ as raw material

\[ \text{ZnO + Cr}_2\text{O}_3 \rightarrow \text{ZnCr}_2\text{O}_4 \]

(2) formation of MgAl$_2$O$_4$ using Al$_2$O$_3$ and MgO as raw materials

\[ \text{Al}_2\text{O}_3 + \text{MgO} \rightarrow \text{MgAl}_2\text{O}_4 \]
2.2.2 Sol-gel method

This chemical process consists of mainly two parts, i.e., sol formation and gel formation. A sol is a dispersion of the solid particles in a liquid where only the Brownian motions suspend the particles. In general metal salts (nitrate or chloride) and alkaline medium (NaOH, NH₄OH) are used to get the sol. A gel is a state where both liquid and solid are dispersed in each other, which presents a solid network containing liquid components. The heat treatment of gel removes the remaining surfactants (organic or inorganic components) and produces amorphous or nano-crystalline material. This is a low temperature (~100°C) route to prepare good quality material with nano-sized grains and better size uniformity [3, 4].

2.2.3 Mechanical synthesis

A schematic mechanism of the mechanical milling process is shown in Fig. 2.1. We employed Fritsch Planetary Mono Miller P6 (Fig. 2.1(a) or P7 and milling of the powdered material was carried out in non-magnetic 45 ml agate bowl or silicon nitride bowl in the presence of non-magnetic silicon nitride/tungsten carbide balls. The ball to material mass ratio was maintained at 4:1-6:1. The milling was continued in air at rotational speed 300 rpm. During mechanical process, the supporting disc and bowl rotates in opposite directions and subsequently, the balls and materials inside the bowl collide to each other (Fig. 2.1(b)). Mechanical synthesis can be classified mainly into two groups, (1) mechanical alloying, and (2) mechanical milling.

Fig. 2.1 (a) Schematic of the milling machine and (b) rotation of the grinding bowl
2.2.3.1 Mechanical alloying (MA)

This technique refers to the formation of alloys/compounds from elemental precursors in the form of metal, non-metal or compounds. The repeated collision between balls and powders with very high impact deform the powder particles. The competing process of deformation, fracture and welding during room temperature (without any external heat treatment) milling produces a micro-structural refinement at the grain boundaries and finally, produces desired compound with grain size micron to nanometer scale [5, 6].

2.2.3.2 Mechanical milling (MM)

This technique refers to the process of milling of pure metals or compounds which are structurally single phased before milling and grain size micrometer scale. It can produce the materials of different structural phases, i.e., nano-crystalline and amorphous materials. Except the starting materials, mechanical milling is similar to the mechanical alloying. The materials obtained by mechanical alloying or mechanical milling may contain a significant amount of structural disorder [7]. Mechanical alloying and mechanical milling of materials are complex stochastic processes which depend on many factors, for instance milling atmosphere, chemical composition of the mixed powder, milling tools, etc [8, 9]. The amount of impurity and defect can be controlled up to certain extent by controlling certain parameters during milling process. Thermal activated grain growth kinetics, e.g., re-crystallization process, can be investigated by subsequent annealing of the mechanical milled/alloyed material [10, 11].

It is worthy to mention that we have identified very minor traces of Si (< 1 atomic %) and W (<0.2 atomic %) in the samples with milling time up to 300 hours. For samples with lower milling time, the contaminants are further less or almost negligible. This is due to proper controlling and monitoring of the milling process. We do not expect significant impact of the minor non-magnetic elements on the magnetic properties of the milled samples. However, these non-magnetic contaminants increase disorder at the grain boundaries of the particles.

2.3 Materials characterization techniques

2.3.1 Powder X-ray diffraction (XRD)

The crystalline structure of the samples was identified using room temperature XRD measurements by X-Pert PANalytical diffractometer. The XRD pattern of each sample was recorded using CuKα radiation in the 2θ range 10°-90° with step size 0.01°. The interaction of
x-ray with crystalline sample is governed by Bragg’s law:

\[ 2d_{hkl} \sin \theta = n\lambda \]  \hspace{1cm} (2.1)

Here, \( d_{hkl} \) is the distance between crystal planes defined by the miller indices \((hkl)\), \( \lambda \) is the wavelength of the incident X-ray beam, \( n \) is an integer. According to Bragg’ law, x-ray diffraction can be visualized as x-rays reflecting from different series of hkl planes (Fig. 2.2). The path differences introduced between a pair of waves traveled through the neighboring crystallographic planes are determined by the \( d_{hkl} \). As the total path difference is equal to \( n\lambda \), the constructive interference will occur and a group of diffraction peaks can be observed and give rise to x-ray pattern.

![Schematic illustration of X-ray diffraction on crystal planes](image)

**Fig. 2.2 Schematic illustration of X-ray diffraction on crystal planes**

### 2.3.1.1 Crystalline size and lattice strain

The peak broadening in XRD pattern for nanomaterials is the result of the finite size effect and grain boundary disorder. Additionally, some other factors such as inhomogeneous lattice strains, variations in the lattice constants from one crystallite to another and structural disorder can also yield the broadening of the diffraction peaks. The crystalline size is roughly calculated by Debye-Scherrer’s equation,

\[ <d> = 0.89\lambda/\beta \cos \Theta \]  \hspace{1cm} (2.2)
where \( <d> \) is the average crystallite (grain) size, \( \lambda = 1.54056 \, \text{Å} \) for Cu K\( \alpha \) radiation, \( 2\theta \) is the peak centre position, \( \beta \) is the full width at half maximum of the peak. The crystallite size \( (d>) \) and lattice strain \( (\varepsilon) \) are more precisely calculated using **Williamson-Hall** [12] equation \( \beta_L = 0.89\lambda/d\cos\theta_C \), \( \beta_G^2 = 8\pi (\tan^2\theta_C)(\varepsilon_{rms})^2 \). \( \beta_{hkl} \) is the integral width (defined as the peak area divided by peak height) of (hkl) peak. The \( 2\theta_C \) (peak center in degree) and \( \beta_{hkl} \) values were obtained by fitting the XRD peak profile Fig. 2.3 (a) to a Pseudo-Voigt function [13]:

\[
V(x) = a \left\{ \frac{c}{1+(x-x_0/b)^2} + (1-c) \exp \left[ -\frac{1}{2} \left( \frac{x-x_0}{b} \right)^2 \right] \right\}
\]

(2.3)

where \( c \) is the relative contribution of the Lorentz function to the pseudo-Voigt function, \( x_0 \) is the position of the maximum of the function, \( b \) is of half width at half maximum and \( a \) is the normalizing factor. The effective Lorentzian (\( \beta_L \)) and Gaussian (\( \beta_G \)) components of \( \beta_{hkl} \) were obtained from \( \beta_L = \beta_{hkl} - \beta_0 \) and \( \beta_G^2 = \beta_{hkl}^2 - \beta_0^2 \), respectively. \( \beta_0 \) is the integral width of standard Silicon powder taken as the measurement of instrumental broadening. We used at least 6-7 prominent peaks to plot \( \beta_L \cos\theta_C \) vs \( \cos\theta_C \) and \( \beta_G^2 \) vs \( \tan^2\theta_C \) curves and estimated grain size \( (<d>) \) and lattice strain \( (\varepsilon) \) of the sample. A typical fitted graph is shown in Fig.2.3 (b).

**Fig. 2.3** (a) fit of a peak (solid symbol) to pseudo-Voigt function (red line), (b) \( \beta_G^2 \) vs. \( \tan^2\theta \) plot with fit curve (left-down scale) and \( \beta_L \cos\theta \) vs. \( \cos\theta \) plot with fit curve (right-top scale) for different peak positions.
2.3.2 Scanning electron microscope (SEM)

The SEM is a microscope that uses electrons instead of light to form the image. SEM can determine the surface morphology of materials. We have used Hitachi S-3400 model for SEM images of the materials and the schematic is shown in Fig. 2.4.

![Figure 2.4 Schematic internal view of the SEM](Ref. 14)

**Working Principle:** Accelerated electrons in an SEM carry significant amounts of kinetic energy, which is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (produce SEM images), backscattered electrons (determine crystal structures), and characteristic X-rays (used for elemental analysis). Secondary electrons and
backscattered electrons are mostly used for imaging samples, e.g., morphology and topography of samples, contrasts in composition in multiphase samples. The great depth of field and the wide range of magnifications are the familiar imaging mode for specimens in the SEM. Characteristic x-rays are emitted when the primary beam causes the ejection of inner shell electrons from the sample. The back-scattered electrons emitted from the sample may be used alone to form an image or in conjunction with the characteristic x-rays as atomic number contrast clues to the elemental composition of the sample. SEM analysis is considered to be "non-destructive", i.e., X-rays generated by electron interactions do not lead to volume loss of the sample. So, it is possible to analyze the same materials repeatedly.

2.3.3 Energy dispersive analysis of X-ray (EDX)

EDX is a technique that provides a qualitative and quantitative elemental analysis of a sample. The elemental analysis of the samples was carried out using EDX spectrometer (Thermo electron corporation Instrument, USA). When a deeper energy (usually K-shell) electron is emitted, a high energy electron will fall into the deeper energy level to fill the vacancy, which in turn generates X-rays to balance the total energy. The emitted X-ray shows a characteristic energy spectrum, which is unique to the specific element of the sample. The elemental analysis can be carried out using different modes of EDX:

1. Spectrum analysis
2. X-ray mapping
3. Point & shoot analysis
4. X-ray line scan

Sample preparation for SEM: Most of our studied samples are not electrically good conductor. The surface of the specimen used for SEM is made conducting by gold coating. The same specimen is used for recording EDX spectrum. The specimens are in powder or pellet form.
2.3.4 Vibrating sample magnetometer (VSM)

We used VSM (Model: 7404 LakeShore, USA) for room temperature magnetic measurement of the samples, along with high temperature oven (300–1000 K) and low-temperature (77–400 K) cryostat attachment. The general arrangement is shown in Fig.2.5. The magnetizing field (0 to ± 15 kOe) in VSM is provided by an electromagnet. The sample is suspended on a non-magnetic rod, which vibrates vertically over amplitude of perhaps 1.5 mm, at a frequency of 45 Hz. The pick-up coils are connected in pull-push. As the sample ascends, both the coils produce the same electrical polarity. The induced ac voltage to the pick-up coils is proportional to sample’s magnetic moment and the induced voltage is amplified using an extremely high-gain lock-in amplifier for better analysis. The rectified output is then applied to a computer and the operation and data processing are all controlled by it. A typical measurement of a sample is taken in the following manner.

Fig. 2.5 Schematic diagram of VSM (model: Lakeshore -7404)
Before magnetic measurement of a sample, the VSM was de-gaussed to remove the remanent field and calibrated using standard Nickel sample.

The sample holder was properly placed between the pole gap of the electromagnet. Then, magnetic measurement with field (at room temperature) or temperature variation (at constant field) was started with proper sequence.

The quality of magnetic data is seen in online plot and continued the measurement.

We mention that low temperature (5 K-300 K) and high magnetic field (0 to ± 50 kOe) dc magnetization for some samples was measured using MPMS (Quantum Design, USA). Saturation magnetic moment ($M_{sat}$) was estimated by extrapolating the magnetization (M) to the 1/H zero limit. The ferromagnetic ordering parameter, i.e., spontaneous magnetization ($M_S$), of the samples was calculated by extrapolating the high field M(H) data to M axis at H = 0 value.

2.3.5 Broadband dielectric spectrometer (BDS)

We have used dielectric spectrometer (model: Novocontrol Technology, Germany) with Alpha-analyzer for dielectric studies (Fig. 2.6).

![Fig. 2.6 Schematic diagram of the used broadband dielectric spectrometer.](image)
2.4 A.C conductivity, impedance and electrical modulus formalism

Fig. 2.7 (a) impedance measurement circuit, (b) phase difference between I(t) and V(t).

The disc-shaped samples (diameter ~ 12 mm, thickness ~ 2-3 mm) were sandwiched between two gold-coated plates that were connected to the spectrometer with special cables (Fig. 2.7 (a)). Dielectric parameters of the material were measured at field amplitude 1 Volt in the frequency range 1 Hz-10 MHz and measurement temperature ranges 298 K - 473 K.

Various dielectric parameters (electrical conductivity (σ), dielectric constant (ε), impedance (Z), electrical modulus (M) and dielectric loss (tanδ)) with frequency can be studied using dielectric spectroscopy. As shown in Fig.2.7 (b), the applied ac voltage V(t) with frequency \( \omega/2\pi \) and the current I(t) flowing through an electrical network [15, 16] is given by

\[
V(t) = V_0 \exp(j \omega t) \tag{2.4}
\]

\[
I(t) = I_0 \exp(j \omega t + \phi) \tag{2.5}
\]

where \( \phi \) is the phase difference between current and applied voltage and \( j = \sqrt{-1} \).

The impedance \( Z(\omega) \) of the circuit is given by

\[
Z(\omega) = V(t)/I(t) = |Z| \exp(-j \phi) = |Z| \cos \phi - j |Z| \sin \phi \tag{2.6}
\]

\[
= Z' - j Z''
\]

where \( Z' \) and \( Z'' \) are the real and imaginary parts of the complex impedance. The relations that relate these two quantities are
total impedance $|Z| = \sqrt{Z'^2 + Z''^2}$ and dielectric loss $\tan \phi = Z'' / Z'$ \hfill (2.7)

The absolute complex permittivity of a material is

$$\varepsilon = \varepsilon' - j \varepsilon'' \hfill (2.8)$$

Dielectric constant or relative permittivity ($\varepsilon_r = \varepsilon / \varepsilon_0$) of the sample is calculated by,

$$\varepsilon_r = C x d / A \varepsilon_0 \hfill (2.9)$$

($\varepsilon_0 = 8.85 \times 10^{-12}$ F/m, d is thickness and A is area of cross section, C is the capacitance).

In the presence of ac electric field, impedance represents a complex combination of various individual circuit elements such as resistance (R), capacitance (C) and inductance (L). The complex plot, i.e., Cole-Cole plot (imaginary vs. real component), of the impedance-related functions, viz., complex impedance, complex admittance, complex electric modulus and complex permittivity, can be used to obtain the information like bulk (grain) resistance, grain boundary resistance, relaxation time and capacitance of the dielectric materials. The grain interior contribution usually observed at high frequency, whereas the contribution of grain boundary observed at lower frequency. It is assumed that electrical net-work of the dielectric materials is a series of the parallel combination of R and C. Fig. 2.8 (a) shows a typical Cole-Cole plot of the imaginary and real components of the impedance with marking for grain resistance ($R_g$) and grain boundary ($R_{gb}$) resistances. Fig.2.8 (b) shows the corresponding series of the parallel RC combinations for grain and grain boundaries, respectively.

![Cole-Cole plot](image)

**Fig 2.8** (a) Idealized common impedance complex plane plot of grain ($R_g$) and grain boundary ($R_{gb}$) in RC parallel and Fig. (b) its equivalent circuit.
Main advantage of electrical modulus formalism is that electrode polarization effects can be suppressed in the analysis of dielectric spectrum. From the physics point of view, electrical modulus corresponds to the relaxation of the electric field in the material when the electric displacement is maintained as constant [17]. It is introduced to describe the dielectric response of non-conducting materials even non-zero conductivity. The electric modulus is reciprocal of permittivity, which used to study interfacial polarization phenomena. The complex electrical modulus can be expressed by following equation.

\[
M^*(\omega) = \frac{1}{\varepsilon^*} = M'(\omega) + i M''(\omega), \quad M' = \varepsilon' / [\varepsilon'^2 + (\varepsilon'')^2], \quad M'' = \varepsilon'' / [\varepsilon'^2 + (\varepsilon'')^2]
\]  
(2.11)

where \(M', M''\) are corresponding to real and imaginary part of the complex electrical modulus.

The electrical modulus is the inverse of complex permittivity,

\[
M^*(\omega) = \frac{1}{\varepsilon^*} = M_\infty [1 - \int_0^\infty e^{-i\omega t} \left\{ \frac{d\varphi(t)}{dt} \right\} dt]
\]  
(2.12)

where \(M_\infty\) is the reciprocal of \(\varepsilon_\infty\), high frequency dielectric permittivity. \(\varphi(t)\) is the relaxation function and is related to relaxation time by the decay function proposed by Kohlrausch, Williams and Watts (KWW) function [18],

\[
\varphi(t) = \exp\left( -t / \tau^\beta \right), \quad 0 < \beta < 1,
\]  
(2.13)

where \(\tau\) is the relaxation time, the value of \(\beta\) decides whether Debye or non-Debye type of relaxation of the sample. If \(\beta > 1\), indicates non-Debye type of relaxation in the system, whereas the value of \(\beta\) is equal to unity for an ideal dielectric.

References