Chapter 2

Experimental and Characterization Techniques

This chapter presents a concise description of materials processing techniques: solid-state reaction route for the polycrystalline bulk and pulsed laser ablation technique for thin films. An overview of swift heavy ion irradiation is also provided. A diversity of experimental techniques engaged to characterize such as structural, electrical and magnetic properties of bulk and thin films have been discussed. In the last instrumentation work (i.e. development of temperature dependent automated dielectric measurement setup and electric field versus polarization (E-P) set up carried out during Ph.D. work is presented.
2.1 Synthesis of Bulk Materials

2.1.1 Solid-State Reaction Technique

Various types of methods are known for the syntheses of the bulk materials such as solid-state reaction [1-6], sol gel [7] and coprecipitation [8, 9]. In the present thesis, the polycrystalline bulk samples of Ti doped Mg$_{0.95}$Mn$_{0.05}$Fe$_2$O$_4$ have been synthesized by solid-state reaction technique. This method of bulk preparation, is also known as ceramic method, has superiority over other methods such as sol gel or coprecipitation technique due to easiness of the process involved in the technique. This process involves various steps such as:

(i) Mixing the required oxide/nitrate powders in appropriate stoichiometric proportion,
(ii) Calcination
(iii) Pelletization
(iv) Sintering

(i) Mixing of Powders

For the preparation of Mg$_{0.95}$Mn$_{0.05}$Fe$_{2-2x}$Ti$_{2x}$O$_4$ samples, the high purity fine powders of MgO, MnO$_2$, TiO$_2$ and FeO were weighed and mixed in stoichiometric proportion.

Powders weighed in the appropriate proportion were mixed thoroughly and ground in highly pure acetone using a mortar and pestle. This process is carried out for several hours in order to achieve the homogeneity of the mixed powder. 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 of calcination procedure is to establish the course of nucleation for the grain growth and felicitates the decomposition of the substituent oxides/carbonates. Mixed powders were kept in alumina crucible and heated in the box 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 Mg$_{0.95}$Mn$_{0.05}$Fe$_{2-2x}$Ti$_{2x}$O$_4$ samples, the
powders were calcinated at 1000 °C. Calcination was repeated 3-4 times with intermediate grinding and every time calcinations temperature was kept 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 required shapes and densities 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 pressure of 5 ton. In our case, pelletization is done in a dye of circular shape of 1 cm and 1.5 cm diameter. The thickness of the pellets were maintained ~3 to 4 mm.

(iv) Sintering

After pelletization of the fine calcinated powder, sintering of the pellet is done at relatively higher temperature and for longer duration than used during calcination. This is 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 Mg$_{0.95}$Mn$_{0.05}$Fe$_{2-2x}$Ti$_{2x}$O$_4$ bulk pellet, the final sintering temperature was kept at 1300 °C for 24 hours followed by slow cooling at the rate of 5 °C/minute. Fig. 2.1 shows the flow chart used for the preparation of bulk samples.
SYNTHESIS METHOD

Solid-State Reaction Technique

AR GRADE OXIDES IN STOICHIOMETRIC AMOUNTS

MgO  MnO₂  FeO  TiO₂

MIXED THROUGHLY AND GRINDED USING MORTAR AND PESTLE FOR ~TWO 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 

Mg₉₅Mn₂₅Fe₂₂₂Ti₇₂O₄

Fig.2.1: Flow chart for the preparation of bulk samples
2.2 Thin Film Deposition: Pulsed Laser Deposition (PLD) Technique

There are many deposition techniques for thin film preparation, such as pulsed laser deposition (PLD) [10-18], chemical vapour deposition (CVD), metal organic chemical vapour deposition (MOCVD) [19-25], DC and RF sputtering [26-30], molecular beam epitaxy (MBE) [31] thermal evaporation [32] sole gel [33] etc. Among the various techniques as mentioned above for thin film deposition; PLD is one of the most commonly used for thin film growth of multicomponent materials. Though, the basic process involved almost in all the techniques is to evaporate the material to provide atomic or molecular species in sufficient background pressure and carry them to the properly heated substrate of particular choice. The choice of substrate for the thin film deposition is guided by the lattice parameter of the compound and substrate as well as the orientation of the substrate. It has been established that high quality epitaxial films of several materials, including multicomponent oxides such as ferrites, multiferroics, ferroelectrics, \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) (YBCO) superconductors, \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) manganites and several other materials can be successfully grown using PLD.\(^{10}\)

The achievement of PLD technique lies in the fact that it maintains the target stoichiometry in the films, which has been found difficult for other conventional techniques such as evaporation, sputtering, etc. Excimer lasers such as XeF (\( \lambda = 352 \text{ nm} \)); XeCl (\( \lambda = 308 \text{ nm} \)); KrF (\( \lambda = 248 \text{ nm} \)); KrCl (\( \lambda = 222 \text{ nm} \)); ArF (\( \lambda = 193 \text{ nm} \)); and F\(_2\) (\( \lambda = 157 \text{ nm} \)) are commercially available and can be used for thin film deposition. It uses a pulsed laser beam, usually but not necessarily, from an ultraviolet excimer laser with pulse energy of about 1 J. The typical duration of the laser pulse is a few tens of nanosecond. Because of such a short duration of pulse, tremendous power (~ 10 - 100 MW/pulse) is delivered to the target. This is because of the nonequilibrium nature of PLD, in the sense that the absorption of energy and ablation takes place in a very short time, usually within a nanosecond, before thermodynamic equilibrium is reached. For the current research work, thin films of \( \text{Mg}_{0.95}\text{Mn}_{0.05}\text{Fe}_2\text{O}_4 \) and Ti doped i.e. \( \text{Mg}_{0.95}\text{Mn}_{0.05}\text{Fe}_{2-2x}\text{Ti}_{2x}\text{O}_4 \) were grown by PLD technique. Typical schematic of the pulsed laser deposition technique is shown in Fig. 2.2.

When a laser beam of energy density above a material dependent critical value is incident on the target, a large amount of energy is deposited in a few hundred-nanometer depth from the surface within a very short time scale. Due to such a transient energy
transfer, temperature of the surface layers is raised to a sufficiently high value (higher than the melting temperature of the material) and thus the melting of material starts at the surface. The process takes place in a very short duration of time scale. This causes a rapid ejection of the laser-induced plasma of materials at right angle from the surface of the target in the forward direction towards the substrate. The plasma plume contains various excited atoms, molecules, ions and neutral species. This plasma quickly expands away from the target towards the substrate where the adiabatic expansion of plasma at the surface of the heated substrate takes place and leads to the growth of the desired thin film.

Fig. 2.2: A schematic view of pulsed laser deposition technique.

While PLD is recognized to transport the stoichiometry from the target to the film, there are several parameters, which immensely influence the growth and properties of thin
films. These parameters are laser energy density falling on the surface of the target, ambient background pressure during and after deposition, pulse repetition rate, temperature of the substrate, choice and orientation of the substrate itself, target to substrate distance etc. Laser energy density is a vital factor, which affects the properties of films. If the energy density is low, the complex target molecules do not evaporate congruently; if very high, droplet kind of particles is deposited on the substrate. The oxygen partial pressure too is vital for the thin film growth of the multiferroics to make up the loss of oxygen in the ceramic target itself or during the course of transfer of the excited species from the target to the substrate.

Thin films were prepared by pulsed laser deposition (PLD) technique from a single-phase bulk target of basic compositions \( \text{Mg}_{0.95}\text{Mn}_{0.05}\text{Fe}_{2-2x}\text{Ti}_{2x}\text{O}_4 \) (15 mm diameter) onto Pt-Si and ITO substrate. The target was processed by conventional solid-state reaction technique. For deposition, a KrF excimer laser (model Lambda Physik, \( \lambda = 248 \text{ nm} \)) set at 20 ns pulse duration, 10 Hz repetition rate and a home-made stainless steel vacuum chamber were used. The thin film deposition was done at UGC-DAE Consortium for Scientific Research, Indore, INDIA. The target was mounted at an angle of 45° to laser beam inside vacuum chamber, where a base pressure of \( 2 \times 10^{-5} \text{ mTorr} \) was achieved through a turbo-mechanical pump. The substrate (10mm \( \times \)10mm) was attached to a stainless steel holder at a distance of 55 mm from the target and is placed parallel to it inside the heater assembly, which is capable to heating the substrate up to 650°C. The target material was rotated at about 10 rpm and the deposition was carried out in an \( \text{O}_2 \) partial pressure of 1 m Torr by keeping the substrate temperature to 450°C. The deposition was performed for \( \sim 25 \text{ min} \). After the deposition, the thin film was cooled slowly to room temperature by turning down the power to the substrate heater and maintaining the oxygen pressure in the chamber to 1 m Torr. The film thickness was measured by profilometer with 0.5 nm resolution.

2.3 Characterization Techniques

2.3.1 X-ray Diffraction

X-ray diffraction (XRD) was first demonstrated by Von Laue in 1912. Today, x-ray diffraction [34] is a routine technique for the characterization of the materials. A rich variety of information can be extracted from XRD. This is appropriate technique for both
form of samples i.e. thin film as well as bulk. Using this technique, one can get the information regarding the crystallinity of the material, nature of the phase present, lattice parameter and grain size [35]. 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 the case of the thin films, the change in the lattice parameter with respect to the bulk gives the idea of the nature of the strain present in the system.

The fundamental of XRD is explained by the Bragg’s equation which places the condition for the constructive interference for the scattered x-ray from the successive atomic planes formed by the crystal lattice of the material. The Bragg’s diffraction condition is formulated by

$$2dsin\theta = n\lambda$$

where $\lambda$ is the wavelength of the incident X-ray, $d$ is the interplaner distance, $\theta$ is the scattering angle and $n$ is an integer-the order of diffraction.

In thin films, X-rays are diffracted by the oriented crystallites at a particular angle to satisfy the Bragg’s condition. Having known the value of $\theta$ and $\lambda$, one can calculate the interplaner spacing. Schematic view of XRD is shown in Fig. 2.3. The XRD pattern can be taken in various modes such as $\theta$ - $2\theta$ scan mode, $\theta$ - $2\theta$ rocking curve, and $\phi$ scan. In the $\theta$ - $2\theta$ scan mode, a monochromatic beam of X-ray is incident on the sample at an angle of $\theta$ with the sample surface. The detector motion is coupled with the X-ray source in such a way that it always makes an angle $2\theta$ with the incident direction of the X-ray beam (Fig. 2.3). The resulting spectrum is a plot between the intensity recorded by the detector versus $2\theta$.

![Fig. 2.3: A representation of x-ray diffraction](image)
In the present work, Bruker D8 Advanced Diffractometer (see Fig.2.4) with Cu K\(\alpha\) \((\lambda = 1.542 \text{ Å})\) was used for the phase detection of bulk powders and thin film at Inter-University Accelerator Centre, New Delhi. The angle 2\(\theta\) was varied from 15 to 80 in steps of 0.05°. The lattice spacing “\(d\)” was calculated using Bragg’s equation (see eqn. 2.1) which is further utilized to calculate lattice constant. The analysis of the XRD pattern was done using Powder-X software [36] at room temperature.

2.3.2 Near Edge X-ray Absorption Fine Structure Spectroscopy

X-ray absorption fine structure (XAFS) refers to the details of how x-rays are absorbed by an atom at energies near and above the core-level binding energies of that atom. When the x-rays hit a sample, the oscillating electric field of the electromagnetic radiation interacts with the electrons which are bound in an atom. Either the radiation will be scattered by these electrons or absorbed, which excite the electrons. A narrow parallel monochromatic x-ray beam of intensity \(I_0\) passing through a sample of thickness \(x\) will get a reduced intensity \(I\) according to the expression:

\[
\ln \left( \frac{I_0}{I} \right) = \mu x
\]  

--- (2.2)
where $\mu$ is the linear absorption coefficient, which depends on the types of atom and the density $\rho$ of the material. At certain energies where the absorption increases drastically, gives rise to an absorption edge.

**Fig. 2.5:** Schematic picture of x-ray absorption phenomenon. An incident beam of monochromatic x-ray of intensity $I_0$ passes through a sample of thickness $t$ and the transmitted beam has intensity $I$.

Each such edge occurs when the energy of the incident photon is just sufficient to cause excitation of a core electron of the absorbing atom to a continuum state, i.e. to produce a photoelectron. Thus, the energies of the absorbed radiation at these edges correspond to the binding energies of electrons in the K, L, M, etc, shells of the absorbing elements. The absorption edges are labelled in the order of increasing energy, K, L, L, L, M, ..., corresponding to the excitation of an electron from the 1s ($2s^{1/2}$), 2s ($2s^{1/2}$), 2p ($2p_{1/2}$), 2p ($2p_{3/2}$), 3s ($3s^{1/2}$), ... orbitals (states), respectively.

An x-ray absorption spectrum is generally divided into 4 sections (see Fig. 2.6): (1) pre-edge ($E < E_0$); (2) x-ray absorption near edge structure (XANES), where the energy of the incident x-ray beam is $E = E_0 \pm 10$ eV; (3) near edge x-ray absorption fine structure (NEXAFS), in the region between 10 eV up to 50 eV above the edge; and (4) extended x-ray absorption fine structure (EXAFS), which starts approximately from 50 eV and continues up to 1000 eV above the edge. The minor features in the pre-edge region are usually due to the electron transitions from the core level to the higher unfilled or half-filled orbitals (e.g., $s \rightarrow p$, or $p \rightarrow d$). In the XANES region, transitions of core electrons to non-bound levels with close energy occur. Because of the high probability of such transition, a sudden rise in absorption process is observed. In NEXAFS, the ejected
photoelectrons have low kinetic energy ($E - E_0$ is small) and experience strong multiple scattering by the first and even higher coordinating shells. In the EXAFS region, the photoelectrons have high kinetic energy ($E - E_0$ is large) and single scattering by the nearest neighboring atoms normally dominates.

![Diagram of X-ray absorption spectrum](image)

**Fig. 2.6:** X-ray absorption spectrum in pre-edge, XANES, NEXAFS and EXAFS regions

In the present work, near edge x-ray absorption fine structure measurement has been done at O-K, Fe-K, Fe-L$_{3,2}$ and Ti-L$_{3,2}$-edges at the soft x-ray beam line 7B1 KIST of the Pohang Accelerator Laboratory (PAL), operating at 2.5 GeV with a maximum storage current of 200mA.

### 2.3.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM), shown in Fig. 2.7, is used for probing of the surfaces and microstructural characterization of the solid samples [37]. This technique is widely used to get information about the topographical features, morphology, phase distribution, crystal structure, crystal orientation and the presence and location of defects. In SEM, as name suggests, the electron beams are moved by the electric field to scan the sample. In this technique, a beam of electron is produced by heating of 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 values. 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 differences 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.

Fig. 2.7: Schematic diagram of scanning electron microscope (SEM)

2.3.4 Atomic Force Microscopy (AFM)

Atomic force microscopy [38] is a powerful technique for probing the surface of the thin film and deducing valuable information of its topological features, fast and accurately. AFM operates by scanning a very sharp and tiny tip attached to the end of a cantilever across the sample surface (Fig. 2.8). The tip approaches the surface of the sample and interacts with it via Van der Waals forces. The interaction translates in a cantilever deflection or a change in the cantilever’s oscillating frequency, depending on the operational mode of the AFM: contact or tapping. The deflection or the frequency changes of the cantilever are detected by an optical system consisting of a laser beam,
which is reflected on the cantilever. The vertical and the horizontal deflections are measured using a split photodiode detector that analyses the reflected beam. The displacement of the cantilever in the three directions is done by means of a piezoelectric scanner, combining independently operated piezo-electrodes, for X, Y and Z direction into a single tube. The two operating modes that have been used, contact-AFM and tapping-AFM, are described in more detail in the following text.

2.3.4.1 Contact Mode AFM

As we have mentioned the changes in the cantilever's deflection are monitored with a split photodiode detector as the tip is scanning the sample surface [39]. A feedback loop maintains a constant deflection between the cantilever and the sample by vertically moving the scanner at each data point to maintain a 'set-point' deflection. By maintaining a constant cantilever deflection, the force between the tip and the sample remains constant. The force \( F \) is calculated from Hook's law: \( F = -kx \), where \( k \) is the spring constant and \( x \) is the deflection. Spring constants usually range from 0.01 to 1.0 N/m, resulting in forces ranging from nN to \( \mu \)N. The distance that scanner moves vertically at each point \((x, y)\) is stored by the computer to form the topographic image of the surface.

2.3.4.2 Tapping Mode AFM

In tapping mode, the cantilever is oscillated near its resonance frequency with the amplitude ranging typically from 20 to 100 nm. The tip lightly 'taps' the surface while scanning, contacting the surface at the bottom of its swing. The feedback loop maintains constant oscillation amplitude by maintaining a constant RMS of the oscillation signal acquired by the split photodiode detector. In order to maintain constant oscillation amplitude the scanner has to move vertically at each point \((x, y)\). The vertical position of the scanner is stored by the computer, to form the topographic image of the sample surface. In the present work, to study topographic and morphology of the thin films, Atomic Force Microscopy (AFM) measurements have been carried out using Nanoscope III a (Digital Instruments) at Inter-University Accelerator Center, New Delhi, INDIA.
2.3.5 Magnetic Force Microscopy (MFM)

The magnetic force imaging is a feature provided by the magnetic force microscope. This method is similar to AFM but the tip of AFM is changed to the magnetic tip of silicon nitride coated with cobalt chromium. Magnetic force Microscope was operated in a phase detection mode whereby a cantilever is forced to oscillate at its resonance frequency and small change in phase due to magnetic interaction is detected. The image obtained is that of the force gradient $dF/dz$ above the sample such that $\Delta \varphi = - Q(dF/dz)/k$, where $Q$ is the quality factor of the cantilever and $k$ is the spring constant. The force acting on the magnetic tip in the $z$ direction is related to the interaction energy $E$, such that $F_z = dE/dz$. If there is no perturbation between the tip and sample then there will be no change in the energy of the system and

$$E = - \int_{tip} M_{tip} H_{sample} = - \int_{sample} M_{sample} H_{tip}$$

(2.3)

where $M_{tip}$ is magnetization of the tip, $H_{sample}$ is the stray magnetic field of sample, $M_{sample}$ is magnetization of sample and $H_{tip}$ is stray magnetic field of tip. This predicts that contrast will only be observed at magnetic domain boundaries. In MFM, measurement tip is first scanned over the sample in order to obtain the topographic information. After each
scan line, the feedback is turned off and the tip is raised above the sample to a user-defined height (20-100nm) to perform a second scan of the surface measuring any far field contribution, such as magnetic forces (at that height only long range forces can be detected, while Vander Walls forces related to the topography are negligible). The topography data acquired during the first scan are used to maintain the tip at a constant height. The existence of magnetic forces shifts the resonant frequency of the cantilever by an amount proportional to vertical gradients in the magnetic forces on the tip. Resonant frequency shifts are very small (from 1 to 5 Hz for a resonant frequency of about 100 Hz) and can be detected either by phase detection mode or by amplitude detection mode. Phase detection measures the cantilever's oscillation phase relative to the piezo-drive, and amplitude detection measures the oscillation amplitude.

![MFM mapping schematics for the magnetic domains of the sample surface.](image)

**Fig. 2.9:** *MFM mapping schematics for the magnetic domains of the sample surface.*

In both cases, the measured signal is proportional to the second derivative of the stray field, emanated from the sample [40]. Phase detection is much superior to amplitude detection and has been used in this thesis. Fig. 2.9 shows how MFM maps the magnetic domains of the sample surface. In the present work, to analyze the domain pattern in the thin films, Magnetic Force Microscopy (MFM) has been carried out on a Nanoscope III a (Digital Instruments) at Inter-University Accelerator Centre, New Delhi, INDIA.
2.3.6 Mössbauer Spectroscopy

Mössbauer spectroscopy is used to get information on the local environment of the 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 is known as Mössbauer effect. For the Mössbauer spectroscopy measurements presented in this work, we used absorption and emission of the γ-ray energy from the first excited state (3/2) of the stable isotope $^{57}$Fe. In the case of $^{57}$Fe spectroscopy the recoil-less 14.4 keV gamma rays are emitted by an excited $^{57}$Fe nucleus obtained from the decay of its parent $^{57}$Co (half life =270 days). The source contains the parent nucleus of the Mössbauer isotope, embedded in a rigid solid matrix (Rh) to ensure a high recoil free factor [41]. 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.

![Fig. 2.10: Mössbauer spectrum showing the simplest case of emitter and absorber nuclei in the same environment.](image)

In order to probe the energy levels of nuclei in different environments, we must scan the energy of the gamma rays and is achieved by moving the source relative to observer. The Doppler effect produces an energy shift in the gamma ray energy by allowing to match the resonant energy levels in the absorber. One of the simplest case is shown in Fig. 2.10 and the spectrum recorded is a plot of the transmission intensity versus source velocity in mm/s.
2.3.6.1 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.

2.3.6.1.1 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

\[ I.S. = \frac{2}{5} \pi Z e^2 \left( R_{ex}^2 - R_{gd}^2 \right) \left[ \frac{e^2}{\Psi_a(0)} \right]^2 - \frac{e^2}{\Psi_s(0)} \]  

--- (2.4)

where \( R_{ex} \) and \( R_{gd} \) are the nuclear radii of the excited and ground state respectively,

\[-e^2\left| \Psi_a(0) \right|^2, -e^2\left| \Psi_s(0) \right|^2\] represent the s-electron densities of the absorber and source respectively and \( Ze \) is the charge on the resonant nucleus. Any difference in the s-electrons environment between the source and absorber thus produces a shift in the resonance energy of the transition called isomer shift (see Fig. 2.11 shows the isomer shift in \(^{57}\text{Fe} \) Mössbauer transition) which and could not be measured directly and so a suitable reference is necessary. In this work, in all the presented results, the isomer shifts are given relative to \( \alpha\text{-Fe} \) 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.

2.3.6.1.2 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 (E. F. G.).

Therefore, the interaction of the nuclear quadrupole moment with the electric field gradient (E. F. G.) at the site of the nucleus gives rise quadrupole splitting (QS) (see Fig. 2.11). The electric field gradient can arise due to the atomic electrons as well as ions, which surround the atoms.

In case of $^{57}$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 $\pm \frac{1}{2}$. This leads to a two-line spectrum separated by the quadrupole splitting. Figure 2.15 shows quadrupole splitting for the Mössbauer transition in $^{57}$Fe.

### 2.3.6.1.3 Magnetic Hyperfine Interaction

A splitting arises through the coupling between the nuclear magnetic moment and the magnetic field at the nucleus, is called magnetic hyperfine interaction or Zeeman splitting (see Fig. 2.11). 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

$$H = -\mu_n I \cdot H = g \mu_n I \cdot H$$

where $\mu_n$ is the nuclear Bohr magneton, $\mu$ is the nuclear magnetic moment, $I$ is the nuclear spin and $g$ is the gyromagnetic ratio. The eigenvalues of Hamiltonian $E_m$ are given by

$$E_m = -g \mu_n H m_I$$

where $m_I = \pm I, I-1, I-2, \ldots, -I$ 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 $^{57}$Fe, the hyperfine splitting for $I = 3/2$ and $I/2$ levels are shown in Fig. 2.11. In ferromagnetic iron metal, the magnetic field at $^{57}$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 programme developed by R. A. Brand [42].

Fig. 2.11: Isomer shift, quadrupole splitting and magnetic hyperfine splitting for the Mössbauer transition in $^{57}$Fe.

2.3.7 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. 2.12. 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 $\text{Mg}_{0.95}\text{Mn}_{0.05}\text{Fe}_{2-2x}\text{Ti}_{2x}\text{O}_4$ bulk samples from 80 K to the room temperature. The
measurements were performed at UGC-DAE Consortium for Scientific Research, Indore, India.

![Vibrating Sample Magnetometer](image)

**Fig. 2.12:** An illustration of Vibrating Sample Magnetometer.

### 2.3.8 Superconducting Quantum Interferometry Device (SQUID)

The SQUID magnetometer is extremely sensitive for measuring small magnetic signal; its sensitivity is up to 10⁻⁸ emu. The key component to the high sensitivity is the SQUID [43], which is super conducting ring with one (RF SQUID) or two (DC SQUID) Josephson junction.
A measurement usually performed in the SQUID (see Fig. 2.13) magnetometer is by moving a sample through the superconducting detection coils, which are located outside the sample chamber and at the center of the magnet. As the sample moves through the coils, the magnetic moment of the sample induces an electric current in the detection coil. Since the detection coils, the connecting wires, and the SQUID input coil form a closed superconducting loop, so any change of magnetic flux of the detection coil will produce a change in the persistent current of the detection circuit, which is proportional to the change in the magnetic flux. The SQUID function as a highly linear current to voltage converter, the variations in the current in the detection coils produces corresponding variations in the SQUID output voltage which is proportional to the magnetic moment of the sample. In a fully calibrated system, measurement of the voltage variations from the SQUID detector as a sample is moved through the detection coils provides a highly accurate measurement of the sample’s magnetic moment. The system can be accurately calibrated using a small piece of material having a known mass and magnetic susceptibility. In the present work PPMS, Quantum design SQUID has been employed to measure the magnetic property of Mg$_{0.95}$Mn$_{0.05}$Fe$_2$O$_4$ thin films at Instrumentation Centre, IIT, Roorkee, India.

The SQUID magnetometer has certain advantages over the VSM, such as it provides better sensitivity (of the order of $10^{-8}$ emu) in the magnetization measurement as compared to the VSM sensitivity (of the order of $10^{-4}$ emu). This is because SQUID magnetometer involves superconducting Josephson junctions, which is very sensitive to any minute change in magnetic flux/voltage. For the operation of these Josephson junctions, things are maintained at liquid helium temperature. Hence, at higher temperature (> 300K), the measurement is difficult as liquid helium starts boiling off. However, in VSM pick up coils do not require cooling for their operation. Therefore, VSM can be operated at higher temperatures also. However, we have used both (VSM and SQUID magnetometer) techniques for the magnetization measurements.
2.3.9 Alternating Gradient Force Magnetometer (AGFM)

The Alternating Gradient Force Magnetometer (AGFM) is widely used in present-days due to its high sensitivity and simplicity [44]. In AGFM, as shown in Fig. 2.14, the sample is mounted to a piezoelectric transducer which oscillates when the sample is subjected to an alternating magnetic field gradient superimposed on the dc field of an electromagnet. The AGFM has a noise floor of $\sim10^{-8}$ emu, however great caution must be taken to avoid large errors in the measurement, such as carefully optimizing the sample position and tuning the frequency. A variety of measurements can be done on AGFM, such as major hysteresis loop, remanance and first order reversal curves. The sample size
that can be used on the AGFM is small, typically 3×3 mm². For the AGFM, the measured moment is very sensitive to sample placement due to the gradient field. To obtain the calibration reading, the sample and the calibration standard must be identical in mass and size. The piezoelectric reed sample holder of the AGFM is very fragile, must operate at the resonance frequency of the sample holder, which depends on the mass of the sample/substrate combination. A new sample usually requires re-tuning of its resonance frequency. When measuring low coercive sample (~ 100 Oe or smaller) it is necessary to reduce the magnitude of the gradient field in order to maintain accuracy.

![Piezo Sensor](image)

**Fig. 2.14:** Schematic diagram of an Alternating Gradient Force Magnetometer (AGFM).

### 2.3.10 Electrical Transport Properties

In the present work, the dc conductivity of the samples was measured using a Keithley electrometer (Model 617) in the temperature range 250 K to 400 K. The temperature was controlled with accuracy of ±50 mK using Lakeshore (Model 340) temperature controller.
2.3.11 Development of Temperature Dependent Automated Dielectric Measurement Setup

The main objective behind the development of automated dielectric setup is to study the behaviour of dielectric constant of different type of materials such as: magnetic materials, ferroelectric and multiferroic materials etc. Such types of materials require accurate measurements of dielectric constant as a function of temperature and frequency. The dielectric constant as a function of temperature measures the unique property of the materials such as ferroelectric property and the transition temperature etc. The dielectric measurement setup was developed to study the temperature dependence of dielectric constant at various frequencies.

The aim was to provide a compact dielectric set up to the researchers at IUAC, New Delhi, with minimum complexity, accurate and reliable measurements. For measuring dielectric constant of ferroelectric materials as well as high dielectric materials at low temperature, a variable temperature probe has been designed; by inserting this in liquid nitrogen (LN2) container, one can vary the temperature from 77 – 500K. The detail of the setup is shown in Fig. 2.15. The system is capable for following type of measurements:

1. Frequency dependent dielectric properties.
2. Temperature (80 K – 500 K) dependent dielectric properties.
3. Temperature (80 K – 500 K) dependent CV measurement.
4. Impedance and Inductance can also be measured in the temperature range 80 K - 500 K.

A calibrated PT100 temperature sensor is placed near to the sample on the copper plate for temperature measurement. A 50 W heater of LakeShore has been inserted in the hole at the base of copper plate. The whole of this sample holder is enclosed by removable stain less steel (ss) cup. When this dipstick cryostat is inserted inside the LN2 dewar, this cup kind of attachment is kept under rough vacuum using a rotary pump. There are ten electrical connections: four for sample, four for sensor and two for heater. Four shielded coaxial cables are for the electrical connections of the sample. These electrical connections travel through the thin SS tube which is about 1 meter in length. All ten connections end as a ten vacuum compatible female BNC connector and then six (four sensor and two heater) connections are terminated in a special D-type male connector through six male
BNC connector from the KF-40. There is sufficient and ample space to keep the samples for the measurement. The sample can be electrically connected using silver paste. The temperature of the sample is controlled using the Lakeshore temperature controller (Model 340) and stabilized within ±50 mK.

This setup is fully automated and program has been written using LabView software.

**Fig. 2.15: Schematic diagram of the cryostat**
Fig. 2.16: Behaviour of temperature dependent dielectric constant ($\varepsilon$) at 100 kHz for BaTiO$_3$.

Typical dielectric measurements carried out using this setup

In order to calibrate dielectric setup, we have performed the dielectric measurement of the BaTiO$_3$ in the temperature range 80K to 450K. Fig. 2.16 shows the variation of the dielectric constant versus temperature for BaTiO$_3$ at 100 kHz. It could be clearly seen from the Fig. 2.16 that BaTiO$_3$ exhibits all four phase expected transitions (i.e. Cubic $\rightarrow$ tetragonal $\rightarrow$ Orthorhombic$\rightarrow$ Rhombohedral). So it can be concluded that the system is working with good accuracy under all required experimental conditions.

The dielectric constant for the bulk sample was calculated by measuring the capacitance of the material. The capacitance as a function of frequency and temperature was measured using Agilent 4284A precision LCR meter. Shielded test leads were used for the electrical connections from the analyzer to the sample in order to avoid any parasitic impedance. The samples were made in the form of rectangular pellets by applying a pressure of 5 tons. Before starting the measurement the samples were heated at 100°C for 1 hour, so as to
homogenize the charge carriers and to remove the moisture content, if any. The surface of
the disks were polished and coated with silver paste that acts as a good contact for
measuring the dielectric properties.

The value of the dielectric constant \( \epsilon' \) was calculated using the formula;

\[
\epsilon' = \frac{C}{C_0}
\]  

(2.7)

where \( \epsilon' \) is the real part of the dielectric constant, \( C \) is the capacitance of the material
inserted between the electrodes and \( C_0 \) is the capacitance of the medium as air or no
medium between the electrodes. The \( C_0 \) for the parallel plate capacitor can be calculated
using the following relation

\[
C_0 = \varepsilon_0 \frac{A}{t}
\]  

(2.8)

For calculating the dielectric constant the dimensions of the pellet used for measurement
were measured with the vernier.

Using equ. 2.7 & 2.8, we can use following relation for the calculating the dielectric
constant

\[
\varepsilon' = \frac{C \times t}{\varepsilon_0 \cdot A}
\]  

(2.9)

where \( \varepsilon_0 \) is permittivity in vacuum \( \sim 8.854 \times 10^{-12} \) \( \text{C}^2/\text{N.m}^2 \), \( C \) is the capacitance of the specimen, \( t \) is the sample thickness and \( A \) is the area of the specimen in sq. m. The
imaginary component of dielectric constant \( \epsilon'' \) is calculated using the formula;

\[
\epsilon'' = \varepsilon' \tan \delta
\]  

(2.10)

where \( \tan \delta \) is loss tangent, proportional to the ‘loss’ of energy from the applied field into
the sample (in fact this energy is dissipated into heat) and therefore denoted as dielectric
loss.

The ac conductivity is calculated from the data of dielectric constant and loss tangent
\( (\tan \delta) \) using the relation

\[
\sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan \delta
\]  

(2.11)

where \( \omega = 2\pi f \).
2.3.12 Development of Electric Field versus Polarization Measurement Setup

Ferroelectric materials are usually defined as irreversibility of the spontaneous polarization by an applied electric field, the observation of the hysteresis is fundamental for the research on ferroelectrics. There are number of experimental setup aimed for measuring these loops, among these setups the Sawyer-Tower [45] circuit is one of the most traditional, which consists of a oscilloscope and a large integrating capacitor in series with the specimen. In the Sawyer-Tower circuit, a sinusoidal or triangular voltage is applied to one of the electrodes of the sample, and the charge Q generated in the sample is detected. The loop obtained using the simple Sawyer-Tower circuit is often distorted because of conduction current and heat dissipation as well. The significance of this measurement can be easily understood by examining the P-E loops for some simple linear devices. The P-E loop for an ideal linear capacitor is a straight line whose gradient is proportional to the capacitance (see figure 2.17(a)). This is because, for an ideal capacitor the current leads the voltage by 90 degrees, and therefore the charge (the integral of the current with time) is in phase with the voltage. For an ideal resistor the current and voltage are in phase, so the P-E loop is a elliptical shape with the centre at the origin (see figure 2.17(b)). If these two components are combined in parallel, we get the P-E loop (see figure 2.17(c)) which is in fact a lossy capacitor, where the area within the loop is proportional to the loss tangent of the device, and the capacitance is proportional to the slope. If we consider less ideal devices such as non linear ferroelectric materials, we would get a P-E loop such as shown in figure 2.17(d). It is well known that there are two charge measurement modes for the system, Sawyer-Tower and virtual ground amplifier mode. In an original Sawyer-Tower circuit there was no provision to eliminate or compensate the different contributions coming from non linear conductivity, capacitance of the samples under study and signal phase difference etc. These contributions deform the shape of the real hysteresis loops to some extent and in some case, may lead to misinterpretation of the ferroelectric character of the materials. Therefore, some modifications in the original Sawyer-Tower circuit are needed. Here, we have developed electric field versus polarization measurement setup, where we have added some new features to compensate the insulating resistance and linear capacitance of the ferroelectric material. This setup is simpler and less expensive than earlier reported, capable to extract quantitative information of coercive field ($E_c$), remanent polarization ($P_r$) and saturation polarization
These parameters are most likely to be of interest to the materials manufacturer and will give a better understanding of the material behavior too.

**Fig. 2.17(a): Ideal linear capacitor response**

**Fig. 2.17(b): Ideal resistor response**

**Fig. 2.17(c): Lossy capacitor response**

**Fig. 2.17(d): Non-linear ferroelectric response**

Fig. 2.18 shows the block diagram of the modified ferroelectric hysteresis loop tracer. A transformer is used to generate high voltage (5 kV (pp), 50 Hz). The applied voltage (V) can be adjusted using the variac transformer. The output of the transformer i.e. high voltage is applied to three different points: (i) to one electrode of the ferroelectric sample (ii) to the network designed for compensating both insulating resistance and linear capacitance of the sample and (iii) to the amplifier /attenuator whose output is directly connected to the X axis of an oscilloscope. The other electrode of the ferroelectric capacitor is connected to an operational amplifier, which is at zero volt potential (virtual...
$V_S$ denotes the voltage across the ferroelectric sample. If $C_S$ is the capacitance of the ferroelectric sample then the charge developed across the ferroelectric sample will be $C_S V_S$.

Since the operational amplifier has infinite input impedance, therefore charge for the ferroelectric sample should come from $C_B$ i.e. capacitor connected between the amplifier's output and non-inverted terminal. The charge from $C_S$ goes into $C_B$ thus producing a voltage which is equal to $q/C_B$, so that the Op-Amp voltage is $-V_B$. Since the charge should be same on both the capacitors, therefore, $V_B = -(C_S/C_B) V_S$. This voltage is proportional to the polarization of the ferroelectric sample and is inverted by an amplifier and than applied to the Y axis of the oscilloscope. Compensation of the linear conductivity of the ferroelectric sample is realized in this circuit by injecting a charge of the opposite sign to that produced by the $V_S$ across the ferroelectric sample. This current is generated by inverting $V_S$ and by applying it across $R_C$. Similarly, the current through the linear capacitance of the sample is cancelled by applying a voltage to $C_C$. In our circuit $R_C$ and $C_C$ have values of 10 kohm and 10 nF. Fig. 2.19 (a - d) shows the ferroelectric hysteresis loop of BaTiO3, PNN and TGS. Fig. 2.19 (c, d) shows the hysteresis loop before and after the compensation at room temperature. The observed value of the ferroelectric parameters i.e. spontaneous polarization and coercive field are in the good agreement with values in the literature.

**Fig. 2.18:** Block diagram of electric field ($E$) versus polarization ($P$) measurement setup.
Fig. 2.19 *Hysteresis loop at room temperature for (a) BaTiO$_3$ and (b) (PbNi$_{1/3}$Nb$_{2/3}$-PbZr$_{0.44}$Ti$_{0.56}$)O$_3$*

Fig. 2.19: *Hysteresis loop of TGS single crystal for (c) Uncompensated and (d) Compensated one.*
2.4. Swift Heavy Ion Irradiation

To understand the swift heavy ion irradiation induced modifications of thin films, we have used Pelletron accelerator and materials science beam line at IUAC, New Delhi.

2.4.1 Pelletron Accelerator

The 15 UD Pelletron, as shown in Fig. 2.20, is a versatile, tandem type of electrostatic heavy ion accelerator. This is installed in a vertical configuration in an insulating tank of 26.5-meter height and 5.5 meter in diameter. In this machine, negative ions are produced and pre-accelerated to $\sim 300$ keV by the cesium sputter ion source known as SNICS (Source of Negative Ions by Cesium Sputtering) (Now it has been replaced by MCSNICS (Multi Cathode SNICS). The pre-accelerated ions are injected into strong electrical field inside an accelerator tank filled with SF$_6$ insulating gas maintained at a pressure of 6-7 atmospheres. The ion beam is selected by injector magnet, which selects the mass of the ion using mass spectroscopy. The ions are mass analyzed by a dipole magnet called injector magnet and are tuned vertically to downward direction. The ions then enter in the strong electrical field inside the accelerator. A terminal shell of about 1.52 meter in diameter and 3.61 meter in height is located at the center of the tank, which can be charged to a high voltage ($\sim 15$ MV) by a pellet charging system. The negative ions on traversing through the accelerating tubes from the column top of the tank to the positive terminal get accelerated. On reaching the terminal they pass through the stripper (foil or gas), which removes electrons from the negative ions and transforms the negative ions into positive ions with high charge state. For very heavy ions (A > 50), the lifetime of the carbon foils used in the stripper are limited to a few hours due to radiation damage. Therefore a gas filled canal or a combination of the gas stripper followed by a foil stripper is used for heavy ions. The transformed positive ions are then repelled away from the positively charged terminal and are accelerated towards ground potential to bottom of the tank. In this way same terminal potential is used twice to accelerate the ion in tandem. Hence, the name given to this accelerator is a Tandem Pelletron Accelerator. The final energy of the emerging ions from the accelerator is given by,

$$E_i = [E_{depot} + (1 + q_i)V]$$  \hspace{1cm} (2.12)

where $E_i$ is the energy of the ions having a charge state $q_i$ after stripping, $V$ is the terminal potential in MV and $E_{depot}$ is the deck potential of the SNICS source. On exciting from
the tank, the ions are bent into horizontal plane using analyzing magnet. This magnet works as an energy analyzer and depending on the dipole magnetic field, ions of particular energy travel in the horizontal direction. The switching magnet diverts the high-energy ion beam into selected beam line of the beam hall. The ion beam kept centered and focused using steering magnets and quadruple triplet magnets. The beam line of the accelerator is in ultra high vacuum (UHV) condition (~10^{-10} mbar). The beam is monitored by beam profile meter (BPM) and the current is observed using Faraday cups. The entire machine is computer controlled and is operated from the control room. The accelerator can accelerate ions from proton to uranium from a few MeV to hundreds of MeV (200 MeV) depending upon the ion.

Fig. 2.20: Schematics of the 15UD Pelletron at IUAC, New Delhi, INDIA.
2.4.2 Materials Science Beam Line

The accelerated beam from the Pelletron accelerator is brought to the beam hall and can be switched to any of the seven beam lines by using the switching magnet. Materials Science beam line is at 15° to the right w.r.t. the zero degree beam line. This beam line has three chambers-high vacuum chambers, ultra high vacuum chamber and goniometry chamber. The high vacuum chamber is a cylindrical shaped multiport stainless steel chamber. A view of the high vacuum chamber is shown in Fig. 2.21 (a). The irradiation experiments were performed in high vacuum chamber (~10^-6 mbar) at room temperature in materials science beam line (see Fig. 2.21(b)). The sample to be irradiated was mounted on the four sides of the target ladder (on copper block). The whole body of the ladder is made of stainless steel and a perforated square copper block is brazed at the end of the ladder. The target ladder is mounted through a Wilson seal from the top flange of the chamber. This top flange is connected to the chamber through a flexible bellow that can be expanding up to 11 cm from its minimum position. A stepper motor in conjunction with suitable mechanical assembly is used to control the up and down motion of the ladder. The beam on the ladder can be observed by observing the luminescence of the beam on the quartz crystal mounted on all sides of the ladder. After the observation of the beam on the quartz, the sample to be irradiated is brought to the same position as that on the quartz by moving the ladder in the desirable position. A CCD camera is attached to one of the ports of the chamber for viewing the sample and the quartz position. The positions can be monitored using close circuit television (CCTV) in the data acquisition room. The magnetic scanner (that can sweep the beam by 15 mm in y-direction and 15 mm in x-direction) ensures the uniform irradiation of samples. A cylindrical enclosure of stainless steel surrounds the sample ladder, which is kept at a negative potential of 120 V. This enclosure suppresses the secondary electrons coming out of the sample during the irradiation. An opening in the suppressor allows the ion beam to fall on the sample. The total number of particles/charges falling on the sample can be estimated by a combination of the current integrator and the pulse counter (Faraday cup) from which the irradiation fluence/dose can be measured.

The counts for the desired ion fluence for each sample can be calculated using the following relation:
2.4.3 Ion Solid Interaction

When an energetic ion passes through the matter, it experiences a series of elastic and inelastic collisions with the atoms which lie in its path. These collisions occur because of the electrical forces between the nucleus and electrons of the projectile and those of the atoms which constitute the solid target. During this collision the energetic ions transfer its energy to nuclei (by elastic atomic collision) and electron (by ionization and excitation) of the target material by two processes:

1. Elastic collision with the target atoms leading to displacement of atoms from their regular lattice sites. This mode of energy transfer is known as nuclear energy loss denoted by \((dE/dX)_n\) or \(S_n\). It is well known mechanism of defect creation in the low energy regime and it has negligible contribution.
2. Inelastic collision with the target electrons causing their excitation/ionization. This mode of energy transfer is referred to as electronic energy loss \( (dE/dX)_e \) or \( S_e \).

Fig. 2.22 shows the schematic of the two mechanisms that occur during the ion-solid interaction.

![Fig. 2.22: Ion-solid interaction: Demonstration of electronic and nuclear energy loss of an ion.](image)

It is well known fact that when a material is bombarded by the heavy ion irradiation, it creates damage zones in the material. When swift heavy ion passes through the material then material in the vicinity of the ions trajectory may be transformed into a disordered state, giving rise to the so called latent track (damage zone created along the path of the swift heavy ion). In case of SHI irradiation, electronic energy loss is the most considerable energy loss process. The emergence of these traces is the result of local electronic energy deposition along the ion path. Therefore, a number of experimental results have shown that the higher electronic excitations can induce the structural modifications. This implies that all the \( S_e \) dependent effects induced in different materials are probably related to the basic energy transfer between the incident ions and the target atoms. Two basic models of microscopic energy transfer mechanism, namely thermal spike and the coulomb explosion have been used to establish the relevant parameters governing the basic energy transfer process.

### 2.4.3.1 Thermal Spike Model

Thermal spike model is based on the transient thermal process. This model was developed to explain the phase transformation after the SHI irradiation. According to this
model the heavy ion irradiation may increase the lattice temperature that induces solid to liquid phase transformation into a localized zone of few nanometer (nm), which is followed by the thermal quenching ($10^{-13}$ K/s) of a cylindrical molten liquid along the ion track. This results in the formation of amorphized latent track. The threshold value for the creation of the latent tracks is associated with the energy needed to induce a liquid phase along the ion path [46, 47].

In this process, the incoming ion gives its energy to the electron gas in $\sim 10^{-17}$ s which is calculated from the collision time of ion with electron. The local thermalization in electronic system will take $10^{-15}$ s to complete. Heat transfer from the electronic to atomic subsystem becomes substantial between $10^{-14}$ to $10^{-12}$ s depending on the magnitude of the coupling (electron-electron coupling and electron-phonon coupling) between the subsystems. The electron-phonon coupling implies the ability of electrons to transfer their energy to the lattice.

2.4.3.2 Coulomb Explosion Model

In the Coulomb explosion model [48, 49], it is assumed that the incoming ions scatter the target electrons and create a column/cylinder of ionized atoms and the excited electrons are ejected by the Coulomb repulsion. The electron excitation energy is rapidly shared with other electrons via electron phonon interaction. The mutual Coulomb repulsion of the ions produces atomic displacements leading to a dense cloud of interstitial atoms and vacancies along the original ion trajectory. This model seems to be well suited for the insulating materials. In metals, which have large electronic mean free path, the free electrons carry away the excitation energy so efficiently that the sample warms up as a whole without considerable atomic motion.

In the present work, the thin films of the $\text{Mg}_{0.95}\text{Mn}_{0.05}\text{Fe}_2\text{O}_4$ ferrites samples deposited on various substrates have been irradiated with 200 MeV Ag ions. The Ag ions were selected to create the columnar defects. In fact, the defect morphology depends upon threshold value of the particular material to be irradiated [50]. The electronic energy loss, $(dE/dx)_e$ of the 200 MeV Ag ion beam for the same samples is about 16.9 keV/nm, which is larger than the $S_{\text{eth}}$. Therefore, there is a possibility of creation of columnar defects /tracks in the materials.
The variation of \( (dE/dx)_e \) and \( (dE/dx)_n \), calculated using SRIM code for 200 MeV Ag ions incident in Mg\(_{0.95}\)Mn\(_{0.05}\)Fe\(_2\)O\(_4\) is shown in Fig. 2.23.

![Graph showing variation of \( (dE/dx)_e \) and \( (dE/dx)_n \) versus energy in Mg\(_{0.95}\)Mn\(_{0.05}\)Fe\(_2\)O\(_4\) for 200 MeV Ag ions.](image)

**Fig. 2.23:** Variation of \( (dE/dx)_e \) and \( (dE/dx)_n \) versus energy in Mg\(_{0.95}\)Mn\(_{0.05}\)Fe\(_2\)O\(_4\) for 200 MeV Ag ions.
References:


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