Chapter 1

Introduction

Material science and engineering have been at the frontier of technological development since the bronze and iron ages. The evolution of material science is always an indicator to man's progress and his urge to improve upon the existing and replace the obsolete with novel materials often results in newer materials and innovations. One prime example of a small but diverse group of materials is the perovskite family. Physicists, chemists and material scientists have shown great interest in these materials, because of properties such as high temperature superconductivity, colossal magneto-resistance and ferroelectricity. A wide variety of fundamental properties like magnetism, ferroelectricity, colossal magneto-resistance and half-metallicity exhibited by perovskite materials make them fascinating from a fundamental perspective as well as an application point of view. They are used in a number of important technological applications such as transducers and memories. A classic example of perovskite structured material is BaTiO$_3$ which is a well known ferroelectric material.

Manganites are mixed valent manganese oxide material with perovskite structure. They are good candidates for research because of their rich phase diagram and colossal magnetoresistance property. They attracted lot of attention due to their properties like charge ordering, orbital ordering, Jahn Teller distortion etc. [1 - 4]. They find numerous applications in the field of technology as magnetic read heads, sensors and switches. The discovery of Giant Magneto-Resistance (GMR) in multilayer films and later the revelation of Colossal Magneto-Resistance (CMR) in perovskites opened the flood gates for renewed research activities in these class of materials. Multiferroicity is the simultaneous
occurrence of ferroelectricity, ferromagnetism and or ferroelasticity. Multiferroic materials are fascinating and have potential applications as memory devices, spintronic devices, sensors and actuators. Hundreds of perovskite materials are magnetic and hundreds of others are ferroelectric. But these properties very seldom co-exist. Manganites were considered as potential material for multiferroic applications because of the leverage with which one can control various properties by compositional changes. Seebeck coefficient of manganites is routinely investigated to explain the transport properties of manganites and not much attention is paid to the fact that such materials can be a potential thermoelectric material with colossal Seebeck coefficient. The magnetoresistance property and its applications are briefly introduced, in this part of the thesis, along with an overview of manganite structure, crystal field splitting and double exchange mechanism. A comprehensive picture of charge ordering, ferromagnetism, ferroelectricity and multiferroism is also included in this chapter. Thermoelectric effects and their applications are also incorporated.

1.1 Magneto-Resistance (MR)

Usually the resistivity of a material depends on temperature only. But for some materials the electrical resistivity depends on the value of applied magnetic field. This property, by virtue of which certain materials exhibit different values of resistance with and without magnetic field, is called magneto-resistance. The physical quantity magneto-resistance (MR) is defined as the ratio of change in resistance to the zero field resistance.

\[ MR = \frac{R(H) - R(0)}{R(0)} \quad (1.1) \]

where \( R(H) \) and \( R(0) \) designate resistance in the applied field \( H \) and zero field respectively. It can be broadly classified into two; Giant Magneto-resistance (GMR) and Colossal Magneto-resistance (CMR). GMR was discovered in 1988 by Baibich \textit{et al} in Paris [5]. It is the phenomenon where the resistance of
specially designed magnetic multi-layers drops dramatically when magnetic field is applied. It is described as giant because it has a much larger effect than that had been previously seen in metals. In 1991 Jin et al discovered very large magneto-resistance in certain type of materials, in their bulk form, called manganites [6]. Manganites are mixed valent manganese oxides. This phenomenon is called Colossal Magneto-Resistance. The word colossal is used to distinguish it from GMR.

1.1.1 Giant Magneto-Resistance (GMR)

GMR has been the subject of a huge international research leading to numerous technological applications. It is observed in magnetic multilayered structures, where two magnetic layers are closely separated by a thin nonmagnetic spacer layer. The first magnetic layer allows electrons with only one spin state to pass through easily. If the second magnetic layer is ferro-magnetically aligned, then that electron can easily find its way to the other end and hence the electrical resistance becomes low. But if the second layer is misaligned, then neither electrons (spin up and spin down) can get through the structure easily and the electrical resistance becomes high. This is illustrated in figure 1.1.

Figure 1.1 Spin alignment effect in GMR
By applying a magnetic field, ferromagnetic alignment can be achieved in the magnetic layers and this diminishes the resistance. The largest application of GMR is in the data storage industry. Other applications are in solid state compasses, automotive sensors, nonvolatile memory and detection of land mines [7].

1.1.2 Colossal Magneto-resistance (CMR)

Colossal magnetoresistance is a bulk property which originates from magnetic ordering and is usually confined to the vicinity of curie temperature (T_c). CMR materials are good candidates for research because of their structural, electronic and magnetic properties, which are interrelated and not very well understood. These materials exhibit a very rich phase diagram, ranging from ferromagnetic metal to antiferromagnetic insulator.

The variation of magnetisation and resistivity in CMR materials with temperature is shown in figure 1.2.

![Figure 1.2 Magnetisation and resistivity vs temperature for CMR material](image-url)
As temperature increases the material undergoes a phase transition from ferromagnetic to paramagnetic (or antiferromagnetic) and a simultaneous metal to insulator transition. These two transitions take place nearly at the same temperature, which is indicative of the existence of a strong relationship between magnetic ordering and transport properties in the case of CMR materials. Manganites, cobaltites and nickelates are examples of materials exhibiting colossal magnetoresistance.

1.1.3 Applications and Limitations of Magnetoresistance

Magneto-resistance already has magnetic appeal. It allows more data to be packed on computer disks. If improvements are made in the interfaces between magnetic layers in thin-film structures, the number of new applications could prove irresistible. For example, it would be possible to make computer operating memories [random access memory (RAM)] that are immune to power disruptions and ionizing radiation. MR motion sensors could be developed to increase the efficiency and safety of home appliances, automobiles, and factories. Magnetoelectronic devices may someday complement or even replace semiconductor electronic devices.

MR recently come out of the laboratory and started finding places in our computers. This is because of the development of “read sensors” for magnetic disk drives [8, 9]. The capacity of disk drives continues to increase rapidly as they shrink in size and thus MR read sensors have become increasingly important. The data are written as tiny regions of magnetisation on a disk covered with a thin film of magnetic material. The information (bits of 1 or 0) is stored as the direction of the magnetisation of these regions. The information is read by sensing the magnetic fields just above these magnetised regions on the disk. As the density gets higher, these regions get smaller, so the fields that must be sensed to read the data become weaker. Read sensors that employ the MR effect provide the best technology currently available for detecting the fields from these tiny regions of
magnetisation. These tiny sensors can be made in such a way that a very small magnetic field causes a detectable change in their resistivity; such changes in the resistivity produce electrical signals corresponding to the data on the disk, which are sent to the computer. It is expected that the MR effect will allow disk drive manufacturers to increase the density at least until disk capacity reaches 10 gigabits per square inch. At this density, 120 billion bits could be stored on a typical 3.5-inch disk drive, or the equivalent of about a thousand 30-volume encyclopedias.

Today's technology uses semiconductor RAM because it is fast, dense, and relatively inexpensive. In semiconductor RAM, data are stored as small regions that have an excess or deficit of electrons. This use of electrical charges to represent data has two serious drawbacks. First, since these charges leak away, the data must be refreshed several times a second by an electrical circuit. Thus, if the power goes off before the data can be written back to the hard disk for permanent storage, they will be lost. Second, because ionizing radiation temporarily destroys a semiconductor chip's semiconducting properties, it can destroy data. Using GMR, it may be possible to make thin-film of magnetic RAM that would be just as fast, dense, and inexpensive. It would have the additional advantages of being nonvolatile and radiation-resistant. Data would not be lost if the power failed unexpectedly, and the device would continue to function in the presence of ionizing radiation, making it useful for space and defense applications.

The application of GMR in motion sensors is also likely to be important in our homes, automobiles, and factories. It provides a convenient way of sensing the relative motion and position of objects without physical contact. Just attach a magnet to one object and a GMR sensor to another. Alternatively, if one of the objects contains a magnetic material such as iron or steel, the object in motion will alter any magnetic field that is present. A GMR sensor could detect these small changes in the magnetic field.
Applications of this effect could become widespread in the industrial, commercial, and military worlds. Here’s a possible list: sensitive detectors for wheel-shaft speed such as those employed in machine-speed controllers, automotive antilock brakes, and auto-traction systems; motion and position sensors for electrical safety devices; current transformers or sensors for measuring direct and alternating current, power, and phase; metal detectors and other security devices; magnetic switches in appliance controls, intrusion alarms, and proximity detectors; motor-flux monitors; level controllers; magnetic-stripe, ink, and tag readers; magnetic accelerometers and vibration probes; automotive engine control systems; highway traffic monitors; industrial counters; equipment interlocks; and dozens of other applications requiring small, low-power, fast sensors of magnetic fields and flux changes [11]. Furthermore, suitable film-deposition processes could also permit fabrication of MR devices on electronic-circuit chips to produce highly integrated MR sensors at low cost and high volumes for mass industrial markets. With its promise for tomorrow’s technologies, MR is bound to attract lots of attention.

Manganites are finding some difficulties in their way to technological applications. Single crystalline samples and epitaxial thin films show intensive magneto-resistance only close to T_c. The larger the T_c, smaller the magneto-resistance. Therefore an improvement of magneto-resistance leads to a decrease of T_c below room temperature. Moreover magnetic fields of several Tesla are required to get CMR. Therefore the main challenge in this field is the synthesis of a material which shows very high value of MR near room temperature with the application of a small magnetic field.

1.2 Manganites

Manganese (Mn), with its five 3d and two 4s electrons, is a transition metal. As such it exhibits variable valency and forms stable compounds in several formal oxidation states. Manganese dioxide (MnO_4^- \cdot O_2^{2-}) or pyrolusite, for example
has a high natural abundance in earth’s crust. It was first recognized as an element by Swedish chemist Karl Wilhelm Scheele in 1774, which was obtained by treating manganese dioxide with hydrochloric acid. Manganese dioxide’s next claim to fame occurred in 1938 with the first observation of antiferromagnetism, two years after its production by Louis Neel. In the second half of twentieth century; another class of manganese oxide called manganites attracted attention of material scientists. 1950, C. H Jonker and J. H van Santen crystallized the first mixed-valence manganites [12]. Manganites are usually perovskite structured manganese oxides showing colossal magnetoresistance property. The mixed valency can be usually obtained by doping alkaline earth in the rare earth manganite. Since rare earth atom is trivalent, manganese has valency 3+ in rare earth manganites. In the case of alkaline earth manganite (eg. CaMnO₃), since the valency of alkaline earth is 2+, Mn has a valency of 4+. Thus in the alkaline earth doped rare earth manganite, Mn ions can have valencies 3+ and 4+ (i.e., mixed valency).

1.2.1 Structure of manganites

Structurally there are three types of manganites namely perovskite manganites, layered manganites and pyrochlore manganites. They are shown in figure 1.3. The perovskite has the general formula ABO₃, where ‘A’ and ‘B’ are cations. Manganites are the three dimensional perovskites. The perovskite structure consists of a lattice of oxygen octahedra with a ‘B’ ion at its centre. ‘A’ cations occupy the vacancies in the octahedra. The perovskite crystal structure is a 3D network of corner shared BO₆ octahedra. Figure 1.4 represents the typical perovskite structure.
Perovskite manganites have the structural formula $\text{A}_{1-x}\text{B}_x\text{Mn}_3\text{O}_9$, where A is the rare earth ion and B is the alkaline earth ion. $\text{La}_{2/3}\text{Sr}_{1/3}\text{Mn}_3\text{O}_9$ is a typical example. In the crystal structure the larger rare earth or alkaline earth ion is at the centre of the cube, the smaller manganese ions at the corners and the oxygen ions at the midpoint of the cube edges (figure 1.5). The structure can be viewed in a different way; manganese at the centre, rare earth or alkaline earth ions at the corner and oxygen at the centre of the face. The Perovskite manganite structure can be regarded as a 3D network of corner shared $\text{MnO}_6$ octahedra with rare earth or alkaline earth metal ions occupying the holes between the octahedral as shown in figure 1.6.
In layered structure, corner shared $\text{MnO}_6$ octahedra forms a double layer with an insulating rock-salt layer of rare earth or alkaline earth ion (e.g. $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$). In pyrochlore structure six $\text{MnO}_6$ octahedra forms a circle with metal ion at its centre (e.g. $\text{Tl}_2\text{Mn}_2\text{O}_7$).

Figure 1.5 Perovskite manganite structure

Figure 1.6 Corner shared network of $\text{MnO}_6$ octahedra in manganite.
1.2.2 Electronic structure and Crystal field splitting

In order to understand the electron transfer mechanism in manganites, we have to consider the electronic structure. The outer electronic configuration of manganese is 3d^5 4s^2. For partially filled d shell, l = 2 and hence isolated ions have 5-fold degenerate orbitals (2l+1), in which we can put up to 10 electrons [2*(2l+1)]. Filling of these levels follows Hund’s first rule to minimize the Coulomb repulsion energy and electrons form a state with the maximum possible spin. The orbitals are d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2} and d_{3z^2-r^2} which are shown in figure 1.7.

![3d orbitals](image)

**Figure 1.7** 3d-orbitals

When a transition metal (TM) ion is put into a crystal, the spherical symmetry of an isolated ion is reduced and consequently some of the orbital degeneracy is lifted. This splitting of degenerate levels is called crystal field splitting. If a TM ion is introduced into a cubic crystal field, the 5-fold orbitally degenerate levels are split into two groups as shown in figure 1.8.
Three levels go down in energy, forming triply degenerate $t_{2g}$ levels and doubly degenerate $e_g$ levels go up [13]. The state with lower energy contains $d_{xy}$, $d_{xz}$, $d_{yz}$ while the higher one is composed of $d_x^2 - y^2$ and $d_{yz}^2 - d_{xz}^2$ [14]. The electron density of $e_g$ orbital is directed towards the negatively charged oxygen ions (called ligands) surrounding the transition metal ion. In contrast, the three $t_{2g}$ orbitals have lobes directed along diagonals in between the ligands as shown in figure 1.9. Hence the $e_g$ orbitals will experience a stronger coulomb repulsion with ligands which raises their energies compared to those of the $t_{2g}$ levels.

![Diagram](image)

**Figure 1.8** Crystal field splitting of Mn 3d orbitals

There exists another contribution to the CF splitting besides the point charge contribution. This is the so called covalency contribution, due to hybridization of the d- orbitals of the TM ion with the p orbitals of the ligands. Due to this hybridization a mixing of these orbitals occurs, which causes the splitting of the d and p levels [15]. The $e_g$ orbitals have a rather large overlap and hence a strong hybridization with the p- orbitals of oxygen occurs (directed towards the TM ions) leading to the so called $\sigma$ - orbitals. Consequently the mixing of $e_g$ and p- orbitals will be strong and gives a corresponding upward shift of the $e_g$ levels.
The hybridization of the $t_{2g}$ orbitals with the corresponding $p$-orbitals of the ligands is smaller than that of the $e_g$ orbitals. The overlap of $p\sigma$ - orbitals with the $t_{2g}$ orbital is zero. The remaining overlap between the $t_{2g}$ orbitals and $p$ - orbitals is known as $\pi$- hybridization. This overlap is permitted by symmetry but it is smaller than the $\sigma$- overlap of $e_g$ orbitals. Thus both of the contribution to the CF, Coulomb repulsion with ligands and $\pi$- $d$ hybridization causes the splitting of $d$- levels in a cubic crystal field.

From the formal valency of a TM in a given compound, the number of $d$ electrons left on the ion is found and these electrons may be put in the CF - split levels, one after another following Hund’s rule (i.e., putting as many electrons with parallel spins as possible). If total number of $d$ - electrons $n_d \leq 3$, then, the total spin of the ion will be $S= n_d/2$. However if we have four $d$ - electrons ($n_d=4$) a problem may arise. If the fourth electron is placed with the spin parallel to those of the first three electrons (i.e according to Hund’s rule), then we should place it in

Figure 1.9 $d$ orbital orientation with ligand oxygen atoms
a higher lying $e_g$ level, which costs us an energy $\Delta_{\text{CF}}$. Alternatively, the fourth electron could be put on one of the lower levels with opposite spin violating Hund's first rule.

Both these situations are met in practice. The first one leads to the so called high – spin state of a TM ion, whereas the second one to the low spin state. The relative stability of one state with respect to another is determined by the ratio of the CF splitting $\Delta_{\text{CF}}$ and the Hund's rule stabilization energy (which may be described as an on site ferromagnetic exchange interaction - $J_H \sum_{\alpha, \beta} S_i \alpha S_i \beta$ where $i$ is the site – index and $\alpha$ and $\beta$ are indices of different d- orbitals). If $\Delta_{\text{CF}} > J_H$, then it would be favourable to form a low - spin state, occupying the lowest CF level at the expense of Hund's rule exchange. In the opposite case the high spin state will be stabilized. Mn $^{3+}$ (d$^4$) has a high spin state.

1.2.3 Orbital degeneracy and Jahn -Teller effect

Crystal field splitting is not the end of degeneracy lifting. In mixed valent manganese oxide the Mn$O_6$ octahedra undergo a deformation called Jahn teller distortion (figure 1.10). Jahn teller theorem states that “any non linear molecule with an electronically degenerate state will undergo spontaneous deformation so as to reduce symmetry, lower energy and thereby attain stability”. In simple terms it is the degeneracy of the spin up and spin down states (in systems without magnetic order). All the other types of degeneracy including orbital degeneracy are forbidden and should be lifted by the corresponding decrease of symmetry. The essence of the theorem is that there is always a perturbation reducing the symmetry with a linear term representing the splitting of the degenerate levels (an energy gain) and a quadratic term representing the energy loss.

Following the standard perturbation theory of degenerate levels in quantum mechanics, the energy of the system as a function of perturbation ‘u’ has the form
\[ E(u) = -gu + \frac{Bu^2}{2} \] (1.2)

**Figure 1.10** Jahn – Teller distortion in manganites

Since the neighbouring TM ions have common ligands (e.g., oxygen), a local JT deformation around one centre interacts with the corresponding deformation, giving rise to correlated displacements. Consequently, the symmetry of the crystal is further reduced. This is known as Cooperative Jahn Teller Effect (CJTE) or as orbital ordering [16, 17]. Jahn-Teller distortion is possible only when there is an electron in the \( e_g \) level. So in the case of manganites, Mn\(^{3+} \) is Jahn-Teller active and Mn\(^{4+} \) is Jahn-Teller inactive.

### 1.2.4 Tolerance factor

The extent of deformation of MnO\(_6\) octahedron can be expressed as a geometrical quantity called tolerance factor. It is defined as the ratio of distance between rare earth or alkaline earth ion and oxygen ion to \( \sqrt{2} \) times that between Mn ion and oxygen ion (equation 1.3). For a perfect cubic structure \( t=1 \). The properties of manganites strongly depend on tolerance factor [18].
Jonker and Van Santen considered that, for the observed simultaneous good electrical conductivity and ferromagnetism, migration of electrons with their spins unpaired from Mn$^{3+}$ to Mn$^{4+}$ sites is a necessity [12]. This idea was put forward and developed into the double exchange model [19] by Zener (1951). In mixed valent manganites, Mn$^{3+}$ has e_g electron while Mn$^{4+}$ has t_{2g} electrons only. Consider an oxygen ion in between Mn$^{3+}$ and Mn$^{4+}$ in a system of overlapping Mn-O- Mn molecular orbital with delocalized electrons.
Zener visualized the electron transfer from one Mn ion to the adjacent Mn ion as the transfer of an electron from one Mn to the oxygen, which is in the middle, simultaneously with the transfer of an electron from the central oxygen to the other Mn ion as shown in figure 1.12. As two simultaneous processes are involved, this model is called double exchange. The configurations of the system before and after the process are given in figure 1.13.

\[ \psi_1 = \text{Mn}^{3+}\text{O}^2\text{Mn}^{4+} \quad \text{and} \quad \psi_2 = \text{Mn}^{3+}\text{O}^2\text{Mn}^{4+}. \]

A necessary condition for this degeneracy is that the spins of the two Mn d-shells (spin of the localized t_{2g} electrons) point in the same direction because the carrier spin does not change in the hopping problem and Hund’s coupling punishes anti-alignment of unpaired electrons. In the double exchange mechanism, hopping of itinerant electron takes place from Mn^{3+} to Mn^{4+} via oxygen and the electrons hop easily along the bonds between the pair of ferro-magnetically ordered Mn^{3+} (t_{1g} e_{g}^0) and Mn^{4+} (t_{2g}) ions, while its motion is hindered between disordered spins due to Hund’s coupling [20].

The motion of e_{g} electrons is thus dependent on the relative spin orientation of the localized t_{2g} moments, which is described by the so called transfer integral:

**Figure 1.13 Degenerate configurations in double exchange**

From figure 1.13, it is clear that the two configurations are degenerate. Due to degeneracy, no activation energy is required for electron hopping. The two states, which are degenerate in energy, are \( \psi_1 = \text{Mn}^{3+}\text{O}^2\text{Mn}^{4+} \) & \( \psi_2 = \text{Mn}^{3+}\text{O}^2\text{Mn}^{4+} \).
\[ T_{ij} \propto \cos(\phi_{ij}/2) \]

where \( \phi_{ij} \) is the angle between moments \( i \) and \( j \); \( T_{ij} \) has of course a maximum when \( i \) and \( j \) are parallel to each other and a minimum when they are anti-parallel \([20, 21]\). The double exchange can quantitatively explain parts of the co-relation between electrical conductivity, ferromagnetism and doping level in mixed valent compounds, but fails to describe the complete phase diagram. This model can be modified to take into account lattice polarons formed on localization of an \( e_g \) electron on \( Mn^{3+} \) (Jahn Teller Distortion).

It is easily understood from the double exchange mechanism that the transport and magnetic properties of mixed valent manganites are connected to the tolerance factor. If tolerance factor is nearly one, then the \( Mn-O-Mn \) bond angle is nearly 180°. In this case, the hoping amplitude is maximum due to the effective overlapping of the orbitals. Small changes in \( Mn-O-Mn \) angle, induced by the cooperative tilting of octahedral or distortions in the octahedral, cause change in the overlap between \( e_g \) and \( p \)-orbitals and thus affect double exchange. It has been pointed out by Goodenough that ferromagnetism is also influenced by super exchange interaction. In super exchange interaction, virtual hopping of electrons takes place between occupied orbitals leading to anti-ferromagnetic coupling \([14]\).

1.2.6 Low, Intermediate and High Bandwidth Managnites

In double exchange, \( e_g \) levels are the active ones for conductivity. These levels hybridize with oxygen \( p \)-levels constituting the conduction band, whose width is called band width. It depends on the overlap of \( e_g \) orbitals of the \( Mn \) and \( p \) levels of the oxygen \([22]\). The orbital’s overlap decreases with the distortion and the relation between bandwidth \( w \) and \( Mn-O-Mn \) bond angle \( \theta \) has been estimated as \([23]\)
Based on band width, manganites are classified into three namely large band width manganite, intermediate band width manganite and low band width manganite. In large bandwidth manganites (eg. La$_{1-x}$Sr$_x$MnO$_3$), the hopping amplitude of electrons in eg band is believed to be greater than that in other manganites. The metal insulator transition temperature of these manganites is relatively large over a wide doping region. The intermediate bandwidth manganites (eg. La$_{1-x}$Ca$_x$MnO$_3$) have some characteristics of large bandwidth manganites like the presence of a robust ferromagnetic phase [24]. But in some aspects they differ from the large bandwidth manganites like the existence of charge/ orbital – ordered phase. In low bandwidth manganites (Pr$_{1-x}$Ca$_x$MnO$_3$) there is very weak ferromagnetic phase and they exhibit stable charge / orbital – ordered phase for a large doping region. The metallic ferromagnetic phase is not stabilized at zero magnetic field in low bandwidth manganites [25].

1.2.7 Charge ordering in manganites

Charge ordering is a phase transition when atoms with different oxidation states form an ordered superlattice. It is usually present in mixed valent compounds like manganites, ferrites etc. In charge ordering, electrons become localized due to ordering of cations of different charges on specific lattice sites and hence leads to insulating behaviour of the material. Wollan and Koehler discovered the charge ordering in rare earth manganites [26]. Charge ordering competes with double exchange and promotes insulating behaviour. In rare earth manganites Ln$_{1-x}$A$_x$MnO$_3$, x=0.5 usually favours charge ordering state because of equal number of Mn$^{3+}$ and Mn$^{4+}$ states. But various compositions in the range 0.3<x<0.75 also exhibits charge ordering depending on Ln and A ions [27]. Charge ordering arises because the carriers are localized into specific sites below a certain temperature, called charge ordering temperature (T$_{CO}$), giving rise to long range order through out the crystal. At low temperatures, the rare earth manganites
are antiferromagnetically ordered with CE type charge ordering, where Mn$^{3+}$ and Mn$^{4+}$ ions order alternately [27]. Investigations of the charge ordering reveal extraordinary variety in the properties which include their fine sensitivity to the average size of the A-site cations, pressure, magnetic field and electric field [28].

1.2.8 Conduction mechanisms in the insulating phase of manganites

In paramagnetic insulating phase mainly three types of mechanism have been found to rule the conduction process in manganites. They are

1. Thermal activation or band gap model,
2. Variable range hopping model (VRH) and
3. Small polaron hopping model (SPH).

1.2.8.1 Small polarons and Large polarons

A localized electron will always distort its surroundings relative to an unoccupied site simply because of the coulombic interaction of the electron and the surrounding atoms. The potential well produced by this distortion acts as a trapping center for the self-trapped carrier. The quasi particle composed of a self-trapped electronic carrier taken together with the pattern of atomic displacements that produces the self-trapping became known as a polaron because self-trapping was first considered in ionic (polar) materials. The quasi particle (i.e. the electron and the distortion) can move as a whole. The spatial extent of the self trapped states depends on the range of the interaction. In long-range electron-lattice interactions, the self-trapped electronic carrier extends over multiple sites produces large polarons [29]. The multi-site extension of the large polaron results in its itinerant motion. The radius of the large polaron decreases continuously as the strength of the electron-lattice interaction is increased. When electronic carrier is confined to a single lattice position, it is called small polaron.
1.2.8.2 Band gap model

Band gap model is widely employed in most of the semiconductors and insulators [30-32]. There is an energy gap between conduction band and valence band. If the thermal energy is sufficient to overcome the band gap, the electron becomes free to conduct. The expression for resistivity can be written in the following form

$$\rho = \rho_0 \exp\left(\frac{E_A}{k_B T}\right)$$  \hspace{1cm} (1.5)

where $T$ is the absolute temperature, $\rho_0$ is the value of resistivity at infinite temperature, $E_A$ is the activation energy and $k_B$ is the Boltzmann’s constant.

1.2.8.3 Small Polaron Hopping (SPH) Model

In the case of small polarons (deeply trapped electrons), the thermal energy is not sufficient to overcome the deep potential well and to hop out of its site. Then the hopping is possible by a multi-phonon assisted process [33]. The expression for resistivity in SPH model can be obtained in the following section [34-36].

If the charge carrier must overcome an activation energy, $E_A$, to hop to a neighbouring site, the probability for hopping will be proportional to $\exp(-E_A/k_BT)$. From the theory of the random walk, the diffusion constant $D$ can be estimated using this hopping probability, the frequency ($\omega$) with which an attempt to hop is made and the site to site distance ($a$) is given by

$$D = \lambda \omega a^2 \exp\left(-\frac{E_A}{k_BT}\right)$$  \hspace{1cm} (1.6)

where $\lambda$ is the geometrical factor. The mobility $\mu$ is related to the diffusivity through the Nernst-Einstein relation

$$\mu = \frac{eD}{k_BT}$$  \hspace{1cm} (1.7)
But conductivity is given by

\[ \sigma = ne\mu \]  \hspace{1cm} (1.8)

i.e.

\[ \sigma = ne^2D/k_B T \]  \hspace{1cm} (1.9)

Putting value of D from equation (1.6) in equation (1.9) we get

\[ \sigma = \frac{ne^2\lambda\omega a^2}{k_B T} \exp\left(-\frac{E_A}{k_B T}\right) \]  \hspace{1cm} (1.10)

Then resistivity can be written as

\[ \rho = \Lambda T \exp\left(\frac{E_A}{k_B T}\right) \]  \hspace{1cm} (1.11)

where \( \Lambda \) is a constant given by

\[ \Lambda = k_B/\lambda ne^2\omega a^2 \]  \hspace{1cm} (1.12)

Thus in the case of materials obeying SPH model logarithm of \( (\rho/T) \) is proportional to reciprocal of temperature.

**1.2.8.4 Variable Range Hopping (VRH) model**

For a semiconductor or insulator at low temperatures, the predominant conduction mechanism may no longer be by thermally activated hopping to the nearest neighbour (SPH) but by variable range hopping (VRH). At low temperatures, the mechanism with the lowest barrier energy will dominate. Due to randomness in the sample, the hopping site with the lowest barrier energy will not in general be the nearest neighbour. The increased hopping distance will of course reduce the probability that the carrier will tunnel to this position; however, this is always offset by the lower barrier energy at sufficiently low temperatures. The simplest quantitative derivation of the form of variable range hopping is the following [37].
For a given site, the number of states within a range $R$ per unit energy is given by

$$n = \frac{4}{3} \pi R^3 N(E_F)$$

(1.13)

where $N(E_F)$ is the density of localized states.

Thus the smallest energy difference ($\Delta E$) for a site within a radius $R$ is on average the reciprocal of ‘$n$’.

$$\Delta E = \frac{1}{n}$$

(1.14)

i.e.

$$\Delta E = \frac{3}{4\pi R^3 N(E_F)}$$

(1.15)

Thus, the further the carrier hops, the lower the activation energy. The carrier has an electronic wave function exponentially localized on a particular site with a decay or localization length of ‘$\alpha$’. The tunneling probability that the electron will hop to a site a distance ‘$R$’ away will contain a factor $\exp(-2R/\alpha)$. The farther is the distance; the lower is the tunneling probability. Since the hopping favours large $R$ while the tunneling favours small $R$, there will be an optimum hopping distance $R$ for which the hopping probability proportional to $\exp(-2R/\alpha) \times \exp(\Delta E/k_B T)$ is a maximum. This will occur when

$$\frac{1}{R^4} = \frac{8\pi N(E_F)k_B T}{\alpha}$$

(1.16)

Substituting this value for $R$, the hopping probability and thus the conductivity is proportional to $\exp(-(T_0/T)^{1/4})$ where

$$T_0 = C\alpha^2/[k_B N(E_F)]$$

(1.17)

where $C$ is a constant. Therefore the conductivity for variable range hopping can be obtained in the form
\[ \sigma = \sigma_0 \exp \left( -\frac{T_0}{T} \right)^{1/4} \]  \hspace{1cm} (1.18)

and resistivity is given by
\[ \rho = \rho_0 \exp \left( \frac{T_0}{T} \right)^{1/4} \]  \hspace{1cm} (1.19)

where \( \rho_0 \) is the resistivity at infinite temperature.

### 1.3 Multiferroics

#### 1.3.1 Ferroelectricity

Ferroelectric materials display a spontaneous polarisation (at \( E=0 \)) that can be oriented and switched by an electric field, and similarly to ferromagnets, ferroelectrics show hysteresis loop. Contrary to ferromagnets, ferroelectrics need to be insulators. Examples of ferroelectrics are perovskite materials such as barium titanate or lead zirconate titante. The electric polarisation and the magnetisation are influenced by temperature. They are largest at low temperatures and at high enough temperatures (above the so called Curie temperature, \( T_c \)) they vanish. The origin of ferroelectricity is determined by balancing the two factors between the long range coulomb forces (which favour the ferroelectric state) and the short range repulsions of the adjacent electron clouds (which favour non polar cubic structure).

Ferroelectricity is one of the most fascinating properties of dielectric solids. Materials exhibiting ferroelectric properties must be either single crystals or polycrystalline solids composed of crystallites; they must also possess reversible spontaneous polarisation [38]. The polarisation induced by an externally applied field in normal dielectric materials is very small, with the dielectric constant usually less than 100, and its effects on other physical properties are also very small. However, there are a number of crystals with a nonsymmetrical structure that exhibit a large polarisation, with the dielectric constant up to \( 10^5 \), under certain conditions. A ferroelectric crystal shows a reversible spontaneous
electric polarisation and a hysteresis loop that can be observed in certain
temperature regions, delimited by a transition point called the Curie temperature,
$T_c$. At temperatures above $T_c$, the crystal is no longer ferroelectric and exhibits
normal dielectric behaviour. Ferroelectric materials usually, but not always, exist
in a nonpolar state at temperatures above $T_c$. The dielectric constant increases very
rapidly to a very high peak value at $T_c$. This is known as anomalous value. At $T >$
$T_c$, anomalous behaviour follows closely the Curie-Weiss relation

$$\varepsilon_r = \frac{C}{T - T_c}$$

where $C$ is known as the Curie constant. In fact anomalous behaviour always
appears near any transition point between two different phases, even at $T$ below
$T_c$. At the transition points, there are anomalies not only in the dielectric constant
and polarisation, but also in piezoelectric elastic constants and specific heat,
because of the change in crystal structure.

Ferroelectrics have reversible spontaneous polarisation. The word
spontaneous means that the polarisation has a nonzero value in the absence of an
applied electric field. The word reversible refers to the direction of the
spontaneous polarisation, that can be reversed by an applied field in opposite
direction. The spontaneous polarisation $P_s$ usually increases rapidly on crossing
the transition point and then gradually reaches a saturation value at lower
temperatures. The most prominent features of ferroelectric properties are
hysteresis and nonlinearity in the relation between the polarisation $P$ and the
applied electric field $F$.

Immediately below the Curie temperature of a continuous ferroelectric
transition, the crystal spontaneously and continuously distorts to a polarized state.
One would therefore expect the dielectric constant to be anomalously large in the
neighbourhood of $T_c$, reflecting the fact that it requires very little applied field to
alter substantially the displacement polarisation of the crystal. In an ideal experiment the dielectric constant should actually become infinite precisely at $T_c$. A typical hysteresis loop of a ferroelectric material is shown schematically in figure 1.14.

![Ferroelectric hysteresis loop](image)

Figure 1.14 Ferroelectric hysteresis loop

When the field is small, the polarisation increases linearly with the field. This is mainly due to field-induced polarisation; because the field is not large enough to cause orientation of the domains (portion OA). At fields higher than the low-field range, polarisation increases nonlinearly with increasing field, because all domains start to orient towards the direction of the field (portion AB). At high fields, polarisation will reach a state of saturation corresponding to portion BC, in which most domains are aligned toward the direction of the poling field. Now, if the field is gradually decreased to zero, the polarisation will decrease, following the path CBD. By extrapolating the linear portion CB to the polarisation axis (or zero-field axis) at $E$, OE represents the spontaneous polarisation $P_s$ and OD represents the remanent polarisation $P_r$. The linear increase in polarisation from $P_s$ to $P_p$ is mainly due to the normal field-induced dielectric polarisation. $P_r$ is smaller than $P_s$ because when the field is reduced to zero, some domains may
return to their original positions due to the strain situation, thus reducing these domains' contribution to the net polarisation.

For most ferroelectric materials, the component due to the normal field-induced dielectric polarisation is very small compared to the spontaneous polarisation; therefore, for most applications, this component can be ignored. The magnitude of differences between \( P_p \) and \( P_s \) in figure 1.10 is exaggerated for the purpose of clear illustration. The field required to bring the polarisation to zero is called the coercive field \( F_c \) (portion OR on zero polarisation axis). \( F_c \) depends not only on temperature, but also on the measuring frequency and the waveform of the applied field. When the field in the opposite direction decreases to zero, the polarisation is reversed, indicating that domains have already been formed before poling and that the motion of the domain walls results in the change of direction of polarisation. The hysteresis arises from the energy needed to reverse the metastable dipoles during each cycle of the applied field. The area of the loop represents the energy dissipated inside the specimen as heat during each cycle.

In general, ferroelectricity is harder to demonstrate in polycrystalline materials composed of crystallites, such as ceramics, than in a single crystal because of the random orientation of crystallites [39]. This is why in some single crystals the polarisation reverses quite abruptly to form a square loop, while in most ceramics the loop is rounded, because of the more sluggish reversal, which is partly due to the axes of the unit cells in the randomized arrangement of the nonuniform crystallites. Ferroelectric materials exhibit ferroelectric properties only at temperatures below \( T_c \) because they are polar; at temperatures above it, they are non polar. Obviously, the shape of the hysteresis loop depends on temperature.
1.3.2 Ferromagnetism

Ferromagnetism arises when the magnetic moments of adjacent atoms are arranged in a regular order i.e. all pointing in the same direction. The ferromagnetic substances thus possess a magnetic moment even in the absence of the applied magnetic field. This magnetisation is known as the spontaneous magnetisation, and it is stable only below a critical temperature, called the Curie temperature. Also, the spontaneous magnetisation decreases as the temperature increases. But above Curie temperature, the regular order disappears (i.e. the atomic magnetic moments lie randomly oriented) and the substance becomes paramagnetic. P. Wiess has developed a simple theory to account for these features of ferromagnetism. According to which i) a ferromagnetic specimen contains, in general, a number of small regions, called domains, which are spontaneously magnetised [40-42]. The magnitude of the spontaneous magnetisation of the specimen is determined by the vector sum of the magnetic moments of individual domains. ii) within each domain, the spontaneous magnetisation is due to the existence of a molecular field which tends to produce parallel alignment of the atomic dipoles (despite the effect of thermal energy). Further, this internal field is equivalent to a magnetic field \( H_m \), which is proportional to the magnetisation \( M \) within a domain; that is

\[
H_m = \lambda M. \tag{1.21}
\]

where \( \lambda \) is a constant independent of temperature, called the molecular field constant or Wiess constant. Thus, if \( H \) is the external magnetic field, the effective field acting on an ion or atom is given as

\[
H_{\text{eff}} = H + \lambda M. \tag{1.22}
\]

There exists a critical temperature known as the ferromagnetic Curie temperature, \( \theta_r \), beyond which the spontaneous magnetisation vanishes. \( \theta_r \) is related to the molecular field constant as
\[ \theta_t = \frac{n\lambda \mu^2}{k_B} \]  

where \( \mu \) is the total magnetic moment per atom.

With the help of molecular field Weiss was able to explain the principle features of ferromagnetism, but he did not touch upon the problem of the origin and the nature of this field. Ideas on the nature and origin of this field were first formulated by Heisenberg on the basis of quantum theory. It is proved that the value of molecular field is large and hence it cannot be due to simple dipole–dipole interaction (i.e. due to the magnetic interaction between neighbours). Heisenberg’s explanation for the large value of the molecular field is based on the non magnetic interaction, called the exchange interaction, between atoms. The exchange interaction arises as a consequence of the Pauli’s exclusion principle: because of this principle we can not change the relative orientation of two spins without changing the spatial distribution of charge, clearly indicating that the interaction exists between the two atoms. It is also clear that this interaction depends upon the relative orientation of the electron spins but not on the spin magnetic moments. The energy of the interaction between atoms \( i, j \) bearing spins \( S_i, S_j \) is of the form

\[ E_{ex} = -2J_e S_i S_j \]  

where \( J_e \) is the exchange integral, the value of which is related to the overlap of the charge distributions of the atoms \( i \) and \( j \), i.e. on their interatomic separation: \( J_e \) is positive for somewhat larger interatomic separations and negative for smaller ones. The above expression is called the Heisenberg model of exchange energy [43]. The exchange integral is positive for iron group of atoms and negative for others: a negative value corresponds to anti-parallel spin configuration, and thus favours non magnetism. According to Bethe \( J_e \) is positive for the iron group atoms because there exists a certain critical ratio of the distance \( r_{ij} \) between neighbouring
atoms i, j in these crystals to the radius $r_{3d}$ of the unfilled 3d-shell. The ratio $r_i/r_{3d}$ is larger than 3 for elements like Fe, Co, Ni etc.

Actual specimens are composed of small regions called domains, within each of which the local magnetisation is saturated. The direction of magnetisation of different domains need not be parallel. Domains also form in antiferromagnetics, ferroelectrics, antiferroelectrics, ferroelastics, superconductors and sometimes in metals under conditions of a strong de Hass–van Alphen effect. The increase in the gross magnetic moment of a ferromagnetic specimen in an applied magnetic field takes place by two independent processes:

i) In weak applied fields the volume of domains favourably oriented with respect to the field increases at the expense of unfavourably oriented domains.

ii) In strong applied fields the domain magnetisation rotates towards the direction of the field.

![Figure 1.15 Ferromagnetic hysteresis loop](image)

Ferromagnetic materials have a spontaneous polarisation (at $H=0$) that can be aligned and switched with a magnetic field. Unlike in paramagnetic or diamagnetic materials, the response of the magnetisation to the field is highly non
linear and represents hysteresis as shown in figure 1.15. The coercivity is usually defined as the reverse field $H_c$ that reduces the induction $B$ to zero, starting from saturation.

### 1.3.3 Multiferroism

Multiferroics are materials in which ferromagnetism, ferroelectricity and ferroelasticity occur in the same phase. This implies that they possess spontaneous magnetisation which can be reoriented by an applied magnetic field, spontaneous polarisation which can be oriented by an applied electric field and spontaneous deformation which can be oriented by an applied stress [44]. It is however, customary to exclude ferroelasticity and only consider magnetic and ferroelectric characteristics.

Electricity and magnetism were combined into one common discipline in the 19th century, culminating in the Maxwell equations. But electric and magnetic ordering in solids are most often considered separately—and usually with good reason: the electric charges of electrons and ions are responsible for the charge effects, whereas electron spins govern magnetic properties. There are, however, cases where these degrees of freedom couple strongly. For example, in the new, large field of spintronics, the effects of spins on the transport properties of solids (and vice versa) allow the possibility to control one by the other. The finding of a strong coupling of magnetic and electric degrees of freedom in insulators can be traced back to Pierre Curie, but the real beginning of this field started in 1959 with a short remark by Landau and Lifshitz in a volume of their Course of Theoretical Physics [45].

The situation changed soon thereafter, when Dzyaloshinskii predicted, and Astrov observed, this type of coupling, which is now known as the linear magnetoelectric effect. This was rapidly followed by the discovery of many other compounds of this class and by a rather complete classification of possible symmetry groups allowing for the effect.
Multiferroic materials have attracted many scientists since the discovery of their ancestor nickel boracite \((\text{Ni}_3\text{B}_7\text{O}_{13})\) [46]. Nowadays people are trying to find a simple structure, for instance among the perovskite oxides, in order to have easier access to their fundamental behaviour. These materials can exhibit magnetism and ferroelectricity simultaneously within one phase. The coupling between the magnetisation and electric polarisation give place to magnetolectric (ME) effects, which offer an extra degree of freedom in the design of conventional actuators or storage devices. Interesting applications can be thought of using this coupling, for instance novel multi-state memory devices that allow to write data using electric fields and to read out by means of magnetic fields. In 1992, Cohen and Krakauer used the first principle calculation to learn about the ferroelectric in the best-known perovskite structure materials such as \(\text{PbTiO}_3\) and \(\text{BaTiO}_3\) compounds [47]. They pointed out that both crystals showed Ti \(3d\) – O \(2p\) hybridization, which is very important to stabilize the ferroelectric distortion. This tendency to hybridize requires \(d^0\) ion state (as in Ti\(^{4+}\)). Unfortunately, d orbital occupancy is required for the existing of magnetic moments and magnetic ordering, so it seems that ferroelectricity and magnetism exclude each other. Recently it was found that hexagonal manganites like \(\text{YMnO}_3\), \(\text{LuMnO}_3\) exhibit multiferroic nature [48, 49].
1.3.4 Requirements of multiferroicity

The following limitations indicate why multiferroic materials are so rare.

1. Symmetries

The existence of ferroelectricity can not be separated from the existence of a structural distortion from a highly symmetric phase. This distortion removes the centre of symmetry and the atomic displacements produce a dipole per unit cell and, therefore, a spontaneous electric polarisation. There are 31 point groups that allow the spontaneous electric polarisation and 31 point groups of spontaneous magnetisation as well. 13 point groups (1, 2, 2', m, m', 3, 3m', 4, m'm', m'm'2', m'm'2', 6 and 6m'm') are found in both states, allowing both properties to exist in the same phase. Many candidate materials which are not in fact ferromagnetic and ferroelectric exist in one of the allowed symmetries. Therefore it is unlikely that symmetry considerations are responsible for the scarcity of ferromagnetic, ferroelectric materials.

2. Electrical Properties

Ferroelectric material must be an insulator (otherwise an applied electric field would induce an electric current to flow, rather than causing an electrical polarisation). Ferromagnets are often metals. So the lack of simultaneous occurrence of magnetic and ferroelectric ordering is simply result a dearth of magnetic “insulators”. Also there are very few antiferromagnetic ferroelectrics, even though antiferromagnets are usually insulating materials.

3. Chemistry – “d'-ness”

If there are no d electrons creating localized magnetic moments, then there can be no magnetic ordering of any type—either ferro-, ferri-, or antiferromagnetic. But as soon as the d- shell on the small cation is partially
occupied, the tendency for it to make a distortion, which removes the center of symmetry, is eliminated.

This could be due to the following two factors

i) Size of the small cation – It is determined that for the perovskite oxides the radii of typical d⁰ B site cations are identical with those of typical B site cations with d electron occupation. Hence the size of B cations is not the deciding factor in the existence of ferroelectricity.

ii) Structural distortions- Ferroelectric material must undergo a phase transition to a low temperature phase that does not have a centre of symmetry. This is achieved in conventional perovskite ferroelectrics by an off – centre displacement of the small (B) cation from the centre of the oxygen octahedron. However for cations with certain d orbital occupancies, the tendency to undergo a Jahn - Teller distortion is strong, and will likely be the dominant structural effect. The Jahn–Teller distorted structure might have a lower driving force for off-centre displacement than the otherwise undistorted structure.

1.3.5 Applications of multiferroics

1) Multiferroic materials are of interest because of their potential applications in information storage [50, 51]. The coupling between magnetism and ferroelectricity could be exploited to induce electrical polarisation by the application of magnetic fields, and vice versa.

2) Multiferroic composite structures in bulk form are explored for high-sensitivity ac magnetic field sensors and electrically tunable microwave devices such as filters, oscillators and phase shifters (in which the ferri-, ferro- or antiferromagnetic resonance is tuned electrically instead of magnetically) [52, 53].

3) In multiferroic thin films, the coupled magnetic and ferroelectric order parameters can be exploited for developing magnetoelectronic devices [54, 55].
These include novel spintronic devices such as tunnel magneto resistance (TMR) sensors and spin valves with electric field tunable functions. A typical TMR device consists of two layers of ferromagnetic materials separated by a thin tunnel barrier (~ 2nm) made of a multiferroic thin film. In such a device, spin transport across the barrier can be electrically tuned.

4) In another configuration, a multiferroic layer can be used as the exchange bias pinning layer. If the antiferromagnetic spin orientations in the multiferroic pinning layer can be electrically tuned, then magnetoresistance of the device can be controlled by the applied electric field. One can also explore multiple state memory elements, where data are stored in the electric and the magnetic polarisations [56].

1.4 Thermoelectric Power

1.4.1 Seebeck effect and other thermoelectric effects

In 1821, Thomas Seebeck discovered that a continuously flowing current is created when two wires of different materials are joined together and heated at one end. This idea is known as the Seebeck effect. Thirteen years later Jean Charles Athanase reversed the flow of electrons in Seebeck circuit to create refrigeration. This effect is known as the Peltier effect. This idea forms the basis for the thermoelectric refrigerator. Scottish scientist William Thomson (later Lord Kelvin) discovered in 1854 that if a temperature difference exists between any two points of a current-carrying conductor, heat is either evolved or absorbed depending upon the material.

The thermoelectric power or Seebeck coefficient (S) is defined as the rate of change of thermoelectric potential with respect to temperature. It is usually expressed in $\mu$V/K.

$$ S = -dV/dT $$  \hspace{1cm} (1.25)
The thermoelectric efficiency of a material depends on three factors, namely Seebeck coefficient, electrical conductivity and thermal conductivity [57]. For an efficient thermoelectric material the Seebeck coefficient should be high in order to produce maximum thermoelectric voltage for unit temperature difference, the electrical conductivity should be high in order to reduce Joule's heating as small as possible and the thermal conductivity should be low for maintaining the temperature gradient. The performance parameter (called figure of merit) of a thermoelectric material is given by

\[ Z = \frac{S^2 \sigma}{K} \] \hspace{1cm} (1.26)

where \( S \) is the Seebeck coefficient, \( \sigma \) is electrical conductivity and \( K \) is thermal conductivity. The performance parameter is usually represented as dimensionless figure of merit \( ZT \), where \( T \) is absolute temperature [49]. The value of \( ZT \) near to 1 is considered as a good thermoelectric material. The thermoelectric efficiency of a thermoelectric generator is given in equation (1.27).

\[ \eta = \frac{\text{energy provided to the load}}{\text{heat energy absorbed at hot junction}} \] \hspace{1cm} (1.27)

And the maximum value of thermoelectric efficiency is given in equation (1.28).

\[ \eta_{\text{max}} = \frac{T_H - T_C}{T_H} \cdot \frac{\sqrt{1 + 2T - 1}}{\sqrt{1 + 2T + T_C}} \] \hspace{1cm} (1.28)

where \( T_H \) is the temperature of hot junction, \( T_C \) is that of cold junction, \( Z \) is figure of merit and \( T \) is absolute temperature [58]. From equation (1.28) it is clear that the thermoelectric efficiency depends on figure of merit and hence strongly depends on Seebeck coefficient.

1.4.2 Applications of thermoelectric effect.

The main applications of thermoelectric effect are power generation from waste heat, temperature sensing and eco friendly refrigeration. The power
generation from waste heat reduces global warming and hence thermoelectric power generation technology is called green technology [57].

Thermoelectric modules can also be used as thermocouples for measuring temperature or providing the temperature-sensing element in a thermostat [58]. To measure temperature the thermoelectric circuit is broken so the current quits flowing. When the current ceases, voltage is measured by a voltmeter as shown in figure 1.17. The voltage generated is a function of the temperature difference and the materials of the two wires used. Two wires used to measure temperature in this manner form a thermocouple. Thermoelectric modules can also be used as power generators [59-61]. A thermoelectric generator (figure 1.18) has a power cycle closely related to a heat engine cycle with electrons serving as the working fluid. Heat is transferred from a high temperature heat source to a hot junction and then rejected to a low temperature sink from the cold junction. The difference between the two quantities is the net electrical work produced.

![Figure 1.17 Thermocouple used for measuring temperature.](image)

The voltage output has been increased significantly with the use of semiconductors instead of metal pairs. Some use n-type and p-type materials connected in series for greater efficiency (figure 1.19). N-type materials are heavily doped to create excess electrons, while p-type materials are used to create
a deficiency of electrons. The couple is connected in series electrically and in parallel thermally then integrated into modules. The modules are placed between ceramic plates to offer optimum stability, electrical insulation, and thermal conductivity. The modules can be either mounted in parallel to increase the heat transfer effect or stacked to achieve high differential temperatures. Thermoelectric devices can also be used as refrigerators on the basis of the Peltier effect [59-61]. To create a thermoelectric refrigerator (figure 1.20), heat is absorbed from a refrigerated space and then rejected to a warmer environment. The difference between these two quantities is the net electrical work that needs to be supplied. These refrigerators are not overly popular because they have a low coefficient of performance.

Figure 1.18 A simple thermoelectric generator
1.5 Motivation of the work

Manganites which belong to the perovskite family are technologically important because of its colossal magneto-resistance property. The electrical conductivity and ferromagnetic properties of such manganites were explained in
terms of the double-exchange interaction. However, recent investigations have shown that the double exchange alone can not explain the observed behaviour in these systems, suggesting strong electron–phonon coupling and the average size of the A and B site cations and the mismatch effect play a crucial role. Thus from physics point of view, low and intermediate band width manganites need much more attention, especially in the low temperature studies. Lanthanum ions may be replaced not only by divalent ions but also by others like alkali metal ions. There are a few reports on perovskite manganites doped with monovalent alkali-metal ions. The manganites recently attracted attention of scientific community because of multiferroic property exhibited by Ca doped rare earth manganites. Charge ordering plays a crucial role in the ferro-electricity. In large band width manganites with divalent alkaline earth cation shows charge ordering (equal amounts of Mn$^{3+}$ and Mn$^{4+}$ ions) at doping level $x = 0.5$. In the case of Na doping, for every amount of Na twice amount of Mn$^{3+}$ will be converted to Mn$^{4+}$ and hence even a small amount of Na doping results in a large number of charge carriers and consequently charge ordering can be expected at $x = 0.25$. Thus charge ordering can be easily attained by low doping without distorting the crystal structure considerably. Again low band width manganites exhibit charge ordering for a wide range of doping concentration ($0.3 \leq x \leq 0.5$). Among the low doped manganites, literature on Gd doped manganites is scarce. Thus an investigation on the multi-ferroic properties of low bandwidth and intermediate bandwidth manganites is an interesting proposition not only from a theoretical point of view but also from practical consideration.

One of the alternatives to the present day energy crisis is the so called green technology, in which energy production is based on Seebeck effect. Large Seebeck coefficient, high electrical conductivity and low thermal conductivity are prerequisites for materials with potential for applications. Metals are poor thermoelectric materials because they possess small values of Seebeck coefficient. Insulators display large values of Seebeck coefficient, but are poor electrical
conductors and are not in demand. Therefore semiconductors are considered as ideal thermoelectric materials. From literature it is seen that SrTiO$_3$, a metal oxide with cubic perovskite structure, is a good thermoelectric material, while rare earth inter-metallic compounds, whose 4f levels are close to the Fermi energy and by virtue of their high density of states near the Fermi energy, scatter most of the conduction electrons, are also considered to be good thermoelectric materials. So perovskite structured manganites with large number of atoms per unit cell, large average atomic mass and large coordination number per unit atom, are capable of displaying large Seebeck coefficient. High bandwidth manganites like La$_{1-x}$Sr$_x$MnO$_3$, though they possess large value of electrical conductivity, display very small values of Seebeck coefficient. However, low band width Gd based manganite and intermediate bandwidth Na doped manganites will be materials with potential for displaying a large Seebeck coefficient. Thus an investigation on the thermo electric properties of the above mentioned manganites will be in the right direction in order to develop thermoelectric power generators.

Recently nano size effects on the material properties capture much attention among the scientific community worldwide. The increased surface to volume ratio may affect the magneto-resistance property, especially in the low temperature regime. In order to study the size effects on the transport properties of manganites we attempted a citrate gel synthesis for the Na doped intermediate band width manganites. Dielectric spectroscopy is used to elucidate the different relaxation mechanisms in the polarisation of materials. Impedance spectroscopy studies will help to gather information on the grain and grain boundary contribution of impedance, which has specific importance in the low temperature region. Manganites show hopping of charge carriers via double exchange and super exchange during their ferromagnetic and paramagnetic (or antiferromagnetic) phases respectively. This hopping mechanism along with the interfacial polarisation from grain-grain boundary interface contribute space charge polarisation and hence dielectric and impedance spectroscopic...
measurements of the materials under study will shed light into the different polarisation mechanisms of the manganites. Hence the present investigation has following objectives.

1.6 Objectives of the work

- Synthesis of low bandwidth manganites belonging to the series of Gd$_{1-x}$Sr$_x$MnO$_3$ (x = 0.3, 0.4 and 0.5) by wet solid state reaction method
- Synthesis of intermediate manganites belonging to the series of La$_{1-x}$Na$_x$MnO$_3$ (x = 0.05, 0.1, 0.15, 0.2 and 0.25) by citrate gel method
- Analysis of structural and magneto-resistance studies of Gd$_{1-x}$Sr$_x$MnO$_3$
- Analysis of structural and magneto-resistance studies of La$_{1-x}$Na$_x$MnO$_3$
- Evaluation of the thermoelectric power of the samples Gd$_{1-x}$Sr$_x$MnO$_3$ and La$_{1-x}$Na$_x$MnO$_3$
- Study the electrical properties of samples Gd$_{1-x}$Sr$_x$MnO$_3$ and La$_{1-x}$Na$_x$MnO$_3$
- Evaluation of dielectric parameters using dielectric spectroscopic studies of the manganite samples
- Study the grain and grain boundary contribution of impedance using impedance spectroscopic studies of the manganite samples
- Correlation of results
Chapter 1

References


[45] Landau L and Lifshitz E, *Course of Theoretical Physics, Electrodynamics of*


