Chapter 1

Introduction

1.1 Preamble

Multiferroics are those materials which have two or more different types of long-range electronic or magnetic ordering [1]. The unique coupling among the independent physical parameters of some physical phenomena such as ferroelectricity, ferromagnetism and ferroelasticity leads to a novel rare phenomena in the material (called as multiferroicity), and the system that exhibits at least two from the above is called multiferroic. Recently, designing, developing and investigating the properties of new materials have attracted much interest and attention of researchers. As multiferroics produce new or enhanced phenomena, and provide a unique opportunity to exploit several functionalities in a single material, these materials have recently simulated an outstanding scientific and technological interest within the scientific community.

Magnetoelectrics (ME) is a special class of multiferroics which are well-known for combining two mutually exclusive order parameters, i.e., ferroelectric (stable and switchable polarization) and ferromagnetic (stable and switchable magnetization) order. Initially the polarization and magnetization were thought to be two independent phenomena and could independently encode information in a single multiferroic bit. Later, they were intrinsically coupled to each other. This coupling permits the data to be written electrically and read magnetically which is the basis of FeRAM and MRAM. The ME can further be divided into two categories: (a) single phase ME which involves a direct coupling of ferroelectric and ferromagnetic domain and (b) multiphase ME composite which shows a strain mediated coupling. Unfortunately, the chemical incompatibility and mutual exclusiveness stand as a big hindrance in combining magnetic and electric ordering in the same phase. Hence, they are few in number.

Functional materials with dimensional and spatial confinements have attracted ever increasing attention in modern technology (e.g., nanotechnology). Particularly in electronic devices, it is of tremendous importance to have control over shape, size and interfaces in the fundamental building blocks like semiconductor-based transistors and
ferromagnetic/ferroelectric information media. Moreover, such confinements have also aroused extensive intellectual curiosity (e.g., in nano-science) to investigate unexpected phenomena both experimentally and theoretically. However, the underlying mechanisms and opportunities are still not fully exploited, especially in novel materials recently discovered, due to lack of appropriate synthesis approach, characterization methodology and functionalization strategy. In addition to 3ds approach (i.e., design, development and device) made for ME, some researchers are trying to develop multiferroic polymer nanocomposite because of the versatile applications of polymer based nano-composite over the traditional ceramic composite, where the parameter ‘frequency’ can be exploited for tailoring the frequency tunable device. So the current urge is to design and fabricate materials having a high coupling constant, low dielectric loss and low leakage current. In this way, to achieve rich functionality, one of the very promising approaches is to create novel materials (in the form of compound or in composite) by modifying or combining different physical properties of different compounds in a single composite.

1.2 Introduction

The understanding and control of magnetic interactions at the nano-scale is important for applications in ultra-high density magnetic data storage, memory and spintronic devices. Magnetic nano-particles themselves are used as the active component of ferrofluids, flexible disk recording media, as well as biomedical materials and catalysts. Furthermore, dramatic changes in magnetic property occur when the particle size is reduced to nanometer scale. The magnetic properties of nanoparticles change dramatically when the critical length governing some phenomena (structural, electrical, magnetic etc.) is comparable to the nano-particle size.

With decreasing particle size, an increasing fraction of atoms lies near or on the surface and interfacial regions, making the effect of the surface and interface electronic structure more and more important. In the case of ferromagnetic metals, particularly of the 3d series (e.g. Fe, Ni, Co, etc.), their effective moments are influenced by the details of the band structure.

In the recent years, nano-ferrites have drawn a considerable scientific and technological attention because of their applications in high-density magnetic recording media, magnetic fluids, catalysts, gas-sensor, high-performance electromagnetic and spintronic devices, and
in magnetic hypothermia and drug delivery system. Previous studies reveal that synthesis of nano-ferrites by the mechanical activation route (high-energy ball milling) induces high coercivity in the ferrite powders. Though some work on the effect of activation (milling) time on structural and magnetic properties of MFe$_2$O$_4$ (M=Mn, Ni, Co) have been reported, systematic studies on structural, electrical and magnetic properties of MFe$_2$O$_4$ has not been reported so far. In view of the importance of the nano-sized MFe$_2$O$_4$ for applications, we have synthesized nano-ferrite using planetary ball milling with different milling time, and studied the effect of milling time on structural, electrical and magnetic properties.

PVDF being a promising ferroelectric polymer has drawn considerable attention because of its fascinating properties. The incorporation of nano-ceramics/ferrites in the polymer matrix can show multiferroic properties. To serve this purpose, PVDF-based polymer nano-composite with the incorporation of nano-fillers such as, PZT multiferroic BFO, BFO-BST, MFe$_2$O$_4$ (M=Mn, Ni, Co) etc. can be designed and characterized for suitable applications.

1.3 Ferroics

The word ‘ferro’ signifies to spontaneous response of order parameters to external agents such as temperature, pressure, electric field and magnetic field. The order parameters, magnetization (M), electric polarization (P) and elastic deformation (e) can be activated by the application of electric field (E), magnetic field (H) and stress (S) respectively. Depending on the external agent the materials can be categorized into ferroelectric, ferromagnetic and ferro-elastic. Beside this, the presence of spontaneous order parameters, ferroics can exhibit (a) existence of multiple domain state and (b) hysteresis caused by field induced domain motion (during order parameter reversal).

![Schematic illustration of a hysteresis loop showing the variation of M, e and P with H, S and E respectively.](image_url)

Fig.1.1 Schematic illustration of a hysteresis loop showing the variation of M, e and P with H, S and E respectively.
A hysteresis loop of three primary ferroics (i.e., ferromagnetic, ferroelastic, ferroelectric), their respective order parameter (M, e and P) and the corresponding fields (magnetic field (H), stress and electric field (E)) is illustrated in Fig.1.1.

In some crystals, arrangement of equivalent ferroic sub-lattices lead to macroscopic compensation, and they are called anti-ferroics such as anti-ferroelectrics and anti-ferromagnetics. They have non-primary order parameters. The properties of ferroic materials are often superior to conventional material because of their spontaneous order parameter and large non-linear coefficients. Due to these properties they can be widely used for sensors and actuators. Ferroic materials usually undergo a phase transition from non-ferroic to ferroic state.

1.4 Ferroelectricity

The electrical analogue of the phenomena of ferromagnetism was discovered in 1920 [1a], when it was found that crystal of Rochelle salt (sodium potassium tartarate tetrahydrate) possess spontaneous polarization (dipole moment per unit volume), and the direction of which can be reversed by the application of a strong electric field. This property was called ‘ferroelectricity’, by analogy with ferromagnetism [2-3]. Ferroelectric behavior arises, as a result, competition between long-range forces of ionic charges in the material, which act to stabilize the ferroelectric phase, and short range repulsive force, which favor non-ferroelectric symmetric structure [4-6]. Covalency softens this repulsion and allows the atoms to have average off-centre displacements, and a net polarization. To possess a spontaneous polarization, a crystal must lack a center of symmetry. In addition, there should be at least two equivalent crystallography orientations for different polarization vector so that the spontaneous polarization must be switchable by an applied electric field [7]. Amongst the 32 crystal point groups, 21 crystal classes do not have a center of symmetry and thus (i) have one or more polar orientation, and (ii) possess odd-rank tensor properties [8]. All but one such non-centrosymmetry point group exhibit piezoelectric effect, which is defined as a change in the electric polarity under applied stress, and vice-versa [9]. The piezoelectricity arises from the coupling of strain and polarization when the polarization interacts with applied electric field. Out of the twenty piezoelectric classes, ten possess a unique polar axis, the spontaneous polarization of which depends on temperature. This is
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called pyroelectric effect. Ferroelectric crystals belong to the pyroelectric family, which in addition has a reversible spontaneous polarization. Hence, a ferroelectric must be simultaneously piezo- and pyroelectric.

1.4.1 Ferroelectric Materials

Generally, the ferroelectric crystal has a twin structure consisting of the region, which has spontaneous polarization with negative and positive polarity. This twin structure is known as domain structure. The twin component is called a domain and the boundary between the domains is called domain wall [10]. The ‘up’ and ‘down’ states of the spontaneous polarization in a ferroelectric domain provide the basis for the 0/1 binary logic used in the memory device. Since the 0 and 1 state are equally stable, there is no need to apply a biasing electric field to make the memory configuration ‘non-volatile’. This is particularly useful for application in NVFRAMs (nonvolatile ferroelectric random access memories) as the means of storing information [11, 12]. The non-linear relationship between polarization and electric field is one of the main and dominating characteristics of ferroelectrics [13-14]. Fig. 1.2 shows a typical hysteresis loop (i.e., variation of polarization (P) with the applied electric field (E)) of a ferroelectric material. The polarization reversal of ferroelectrics can be observed by tracing the hysteresis loop. With increasing the applied electric field, domains grow at the expense of other domains.

![Hysteresis Loop](image)

Fig. 1.2: Variation of polarization (P) with applied electric field (E) for a ferroelectric material [2].

This process continues with increasing electric field until the least favorably oriented domains switch to the polar direction most nearly coinciding with the electric field direction. If the linear response is extrapolated to the polarization axis (E=0), the polarization value at the intersection is designated as the
saturation polarization ($P_s$). When the field returns to zero, the polarization does not return back to the initial value. The amount of switchable polarization after removal of an electric field is called the remnant polarization ($P_r$). The horizontal intercept of the hysteresis loop or the field at which the net polarization becomes zero is called the coercive field ($E_c$). At coercive field, polarization reversal occurs, giving a large dielectric non-linearity. The area within a loop is a measure of energy required to reverse the polarization twice. If the temperature is increased, the area of the loop decreases and becomes a straight line at transition temperature ($T_c$) (which is associated with the ferroelectric to paraelectric phase transition). The domain configuration of ferroelectrics is quite complex, and so is their hysteresis loop. Hysteresis loop is strongly affected by many factors, such as lattice imperfections, surface boundary conditions as well as thermal and electrical history. The hysteresis loop parameters (i.e., coercive field ($E_c$), remnant polarization ($P_r$), saturation polarization ($P_s$) etc) are very important for the identification and classification of ferroelectric material.

1.5 Magnetism and Magnetic Materials

The magnetic phenomenon has been known for thousands of years. The magnetic moment of an atom / ion is derived from three main sources: (a) the spin of electrons, (b) electron orbital angular momentum about the nucleus, and (c) a change in the orbital moment induced by an applied external magnetic field. The first two sources give paramagnetic behavior to the magnetization, and the third one gives a diamagnetic contribution.

1.5.1 Classification of Magnetic Materials

In a crystal, the overall magnetic property depends on two factors: (i) the magnetic response associated with each atom, and (ii) the interaction between these magnetic moments. In case, if there are no unpaired electrons around each atom, there will be a zero net magnetic moment associated with them (i.e., both orbital moments and electron spins cancel each other), then the material will show diamagnetic behavior. When there are unpaired electrons, every atom has a net magnetic moment. Depending on the interactions between the magnetic dipoles, the material may show (i) diamagnetism, (ii) paramagnetism (iii) ferromagnetism, (iv) anti-ferromagnetism and (v) ferri-magnetism. Materials in the first two
groups are those that exhibit no collective magnetic interactions and are not magnetically ordered. Materials in the last three groups exhibit long-range magnetic order below a certain critical temperature.

In a paramagnetic material, alignment of adjacent moments is not observed due to thermal fluctuation. In ferromagnetism the adjacent moments are aligned parallel to each other. In anti-ferromagnetic order equal moments are aligned in an anti-parallel way, and ferromagnetic order consists of anti-parallel and unequal moments, resulting in a non-zero net magnetization [15]. The term weak ferromagnetism is used to describe anti-ferromagnetism with a small canting of the spins away from anti-parallel alignment [16]. If a substance is placed in a magnetic field \( (H) \), the magnetic induction \( (B) \) is presented by the equation:

\[
B = \mu_0 (H+M).
\]

The response of a material to a magnetic field is quantified by two parameters: the susceptibility \( \chi \) and permeability \( \mu \), given by the equations, \( \chi = M/H \) and \( \mu = B/H \).

For diamagnetic substances \( \chi \) is small and negative. For paramagnetic material \( \chi \) is small and positive. The most widely recognized magnetic materials are the ferromagnetic materials for which the \( \chi \) is positive and much greater than 1. In anti-ferromagnetic materials, \( \chi \) is positive; its value is comparable to or somewhat less than those of the paramagnetic materials. The susceptibility of many paramagnetic materials varies inversely with temperature and obeys the Curie law, especially at high temperature: \( \chi = C/T \), where \( C \) is the Curie constant. However, for the ferromagnetic and anti-ferromagnetic materials the temperature dependence of susceptibility obeys a modified or generalized law known as Curie-Weiss law, i.e., \( \chi = C/T - \theta \), where \( \theta \) is constant with the dimension of temperature.

Ferromagnetic materials have a very large susceptibility at low temperatures that decreases rapidly with rise in temperature. Above a certain temperature (Curie Temperature \( T_C \)), the material is no longer ferromagnetic but reverts to paramagnetic, where Curie-Weiss behavior is usually observed [17]. For anti-ferromagnetic materials, the value of \( \chi \) increases with rise in temperature up to a critical temperature, known as the Neel temperature (\( T_N \)), above which the material again reverts to paramagnetic behavior. For ferro and anti-ferromagnetic materials, the temperature dependence of \( \chi \) does not follow the simple Curie/Curie Weiss laws. For all materials, the effect of increasing temperature is to increase
the thermal energy, and therefore, there is a natural tendency for increasing structural disorder eventually destroying the long range magnetic order.

The most important class of magnetic material is the ferromagnetic material, whose applications are very diverse, such as transformer, information storage, magnetic bubble memory devices, permanent magnets etc. [18]. In a ferromagnetic material, the macroscopic magnetization is caused by the magnetic dipole moment of the atoms tending to line up in the same direction. There are two phenomenological theories that successfully explain many ferromagnetic properties. One is the Curie-Weiss localized momentum theory and other is the Stoner band theory of ferromagnetism. Weiss [19] postulated that an internal ‘molecular field’ acts in ferromagnetic materials to align the magnetic moments parallel to each other. The origin of this molecular field was later understood to be quantum mechanical spin interaction [20] which causes electron with parallel spins to have lower energy than electrons with anti-parallel spins, all other factors being equal. In this case the exchange interaction is negative. If the exchange interaction is positive, a state with lower energy is attained with anti-parallel alignment of the spins is called anti-

![Image of magnetic dipole ordering](image)

**Fig 1.3: Four types of magnetic dipole ordering in magnetic materials.**

ferromagnetism. At temperatures below $T_c$, the molecular field is so strong that the magnetic moments align even without an external magnetic field. At temperatures higher than $T_c$, the thermal energy, $kT$, is greater than the alignment energy of the molecular field, resulting in a random orientation of the magnetic moment called paramagnetic behavior.
As per the Stoner theory [21], ferromagnetism is also due to the exchange interaction which is minimized if all of the spins are aligned. Opposite alignment of the spins leads to an increase in the band energy involved in transferring electrons from the lowest band state to band state of higher energy. This band energy prevents simple metals from being ferromagnetic. Fig. 1.3 shows the four different types of magnetic dipole ordering in magnetic materials.

A ferromagnetic domain, in which a group of atoms coupled together magnetically, is called a magnetic domain. Magnetic domains can be oriented to produce a spontaneous magnetic field in the absence of the external field. Ferromagnetism disappears, if material is heated to Curie temperature ($T_c$), as inter-atomic coupling restricted and domains then cannot exist. As ferromagnetism tends to concentrate magnetic flux density, they have spontaneous magnetization, as a result of which they have lots of applications such as transformer cores, permanent magnets and electromagnets. In ferromagnetic materials, the incomplete cancellation of the magnetic dipoles in a domain results in lower permanent magnetization [22]. The macroscopic magnetism of ferro- and ferri-materials is the sum of magnetization of the domains which make up the sample [15]. Ferrimagnets are ionic solids, meaning that they are electrically insulating, whereas most ferromagnets are metals (conductors) [18].

1.5.2 Ferromagnetic materials

A ferromagnetic material exhibits a spontaneous magnetic moment, even in the absence of a magnetic field. The left side of Figure 1.4 b shows how the magnetic dipoles order in a ferromagnetic material, while the right side shows the variation in overall magnetization in an applied magnetic field. The laboratory-fabricated ceramic samples typically have no net magnetization due to the presence of domains, which are oriented in different directions to minimize the overall energy of the sample. However, once a magnetic field is applied, these domains try to align and reorient themselves with the magnetic field, in order to minimize their energy, resulting in the hysteresis behavior seen in Fig. 1.4 b. The material starts with no net magnetic moment, and as a positive magnetic field is applied the magnetization increases to a saturation value, known as the saturation magnetization, $M_s$. Saturation magnetization corresponds to the state where all the magnetic dipoles and domains are aligned parallel to one another. When the field is removed the magnetization decreases from
the saturation value to a remnant value, \( M_r \). The coercive field, \( H_c \), is the field required to return the magnetization to zero. If a negative magnetic field applied, then the magnetization will again increase to its saturation value, but in the opposite direction. The properties of the hysteresis loop are determined by the intrinsic material properties. Most magnetic materials are anisotropic in their magnetic properties, meaning that it is relatively easier to magnetize samples along certain crystallographic directions, referred to as the easy axes. A greater degree of anisotropy manifests itself by allowing fewer magnetically easy axes, and therefore requires larger fields to achieve the saturation magnetization and to return to a net magnetization of zero. These highly anisotropic ferromagnetic materials are referred to as hard magnets, whereas ferromagnetic materials with low degrees of anisotropy are referred as soft magnets. Hard and soft magnets are distinguished by the shape of their hysteresis loops. Hard magnets are characterized by broad square-shaped hysteresis loops, with two stable magnetic states, whereas soft magnets have narrow hysteresis loops, allowing for easy switching between magnetic states.

![hysteresis loops](image)

\[ M \]

\[ H \]

\[ M_{\text{sat}} \]

\[ H_c \]

\[ M \]

\[ H \]

\[ M_{\text{sat}} \]

\[ H_c \]

**Fig. 1.4 Schematic ordering of magnetic dipoles in a) paramagnetic, b) ferromagnetic, c) anti-ferromagnetic and d) ferri-magnetic materials.**

The area within a hysteresis loop is equivalent to the energy required to switch between the two magnetic states, and manifests a loss when a material is rapidly switches between the two magnetic states. Hard magnets are typically used in memory storage applications that
require two distinct states that cannot be easily changed, where loss is not an issue. On the other hand, soft magnetic materials find applications in dc power applications, such as transformer cores, where low hysteresis loss is important. Like many material properties, ferromagnetism is a temperature dependent phenomenon. Ferromagnetic materials undergo a phase transition from a high temperature paramagnetic phase, where the magnetic moments within the sample are randomly oriented as a result of thermal motion (Fig. 1.4 a), to a low temperature phase where the dipole moments order parallel to one another (Fig. 1.4 b). This transition temperature is defined as the Curie temperature, $T_c$. Above the Curie temperature the thermal energy, $kT$, exceeds the energy aligning the magnetic moments resulting in a random alignment of the magnetic moments and paramagnetic behavior. Aside from ferromagnetic and paramagnetic behavior, Fig. 1.4 also shows two additional types of magnetic behavior; anti-ferromagnetic and ferromagnetic. In anti-ferromagnetic materials (Fig.1.4c), the dipoles align anti-parallel to one another, resulting in no overall magnetic moment. Ferrimagnetic materials are similar to anti-ferromagnetic materials in that their dipoles align anti-parallel. However, ferrimagnetic materials are typically comprised of more than one magnetic species or sub-lattices, where each of these species align parallel with one another, but anti-parallel with the other species or sub-lattice. Therefore, the opposing moments do not cancel one another out, and there exists a net magnetic moment. Ferrimagnetic materials, similar to ferromagnet, have a spontaneous moment below their Curie temperature and their net magnetization in an applied magnetic field exhibits hysteresis behavior.

1.6 The Weiss theory and Heisenberg exchange interaction

If a hysteresis loop starts with (i) the un-magnetized state of the ferromagnetic material, and (ii) the increase of applied magnetic field in the positive direction, the magnetization increases from zero to a saturation value ($M_s$), because of the motion and the growth of the magnetic domains. When this saturation point is reached, the magnetization curve no longer retraces the original curve when $H$ is reduced. This is because of the irreversibility of the domain wall displacements. When the applied field $H$ decreases to zero again, the sample still retains some magnetization, known as remnant magnetization ($M_r$) because of the existence of some domains still aligned in the original direction of the applied field. The magnetic field needed to drive the magnetization ($M$) to zero is called intrinsic
Coercivity ($H_c$), which represents the ability of a permanent magnet to resist demagnetization. If the field continuously increases in the negative direction, the material will become magnetically saturated, but in the opposite direction, thus switching the magnetization. M-H hysteresis loop (Fig 1.5). To explain the spontaneous alignment of the spins and the hysteresis loop developed in the ferromagnetic materials, a strong internal magnetic field (proportional to the magnetic moment) was assumed which aligns the dipoles even without an external field. Microscopically, there are small regions, called domains, each of them spontaneously magnetized. The magnetic moment of the entire specimen is then the vector sum of the magnetic moment of each domain. Since the direction of each domain may not be parallel, certain domain configurations lead to zero net moment. The application of a relatively small field changes the domain arrangement, and hence an appreciable change in net magnetization. Domain switching under external field produces hysteresis loop. The application of a relatively small field changes the domain arrangement, and hence an appreciable change in net magnetization. Domain switching under external field produces hysteresis loop.

Fig. 1.5: Magnetic hysteresis loop (variation of M verses H) for magnetic materials.[21a]
A ferrite is a type of ceramic compound composed of iron oxide (Fe₂O₃) combined chemically with one or more additional metallic elements. They are both electrically nonconductive and ferrimagnetic, meaning they can be magnetized or attracted to a magnet. Ferrites can be divided into two families based on their magnetic coercivity and their resistance to being demagnetized: hard and soft ferrites. The hard ferrites have high coercivity; they are difficult to demagnetize. They are used to make magnets, for devices such as refrigerator magnets, loudspeakers and small electric motors. The soft ferrites have low coercivity. They are used in the electronics industry to make ferrite cores for inductors and transformers, and in various microwave components. Yogoro Kato and Takeshi Takei of the Tokyo Institute of Technology invented ferrite in 1930. Many ferrites are spinels with the formula AB₂O₄, where A and B represent various metal cations, usually including iron Fe. Spinel ferrites usually adopt a crystal motif consisting of cubic close-packed (FCC) oxides (O²⁻) with A cations occupying one eighth of the tetrahedral holes and B cations occupying half of the octahedral holes. If one eighth of the tetrahedral holes are occupied by B cation, then one fourth of the octahedral sites are occupied by A cation and the other one fourth by B cation and it's called the inverse spinel structure. It's also possible to have mixed structure spinel ferrites with formula [M²⁺₂⁺δFe³⁺δ] [M²⁺δFe³⁺₂⁺δ] O₄ where δ is the degree of inversion.

1.7.1 Soft Ferrite

Ferrites that are used in transformer or electromagnetic cores contain nickel, zinc, and/or manganese compounds. They have a low coercivity and are called soft ferrites. The low coercivity means the material's magnetization can easily reverse direction without dissipating much energy (hysteresis losses), while the material's high resistivity prevents eddy currents in the core, another source of energy loss. Because of their comparatively low losses at high frequencies, they are extensively used in the cores of RF transformers and inductors in applications such as switched-mode power supplies and loop stick antennas used in AM radios.
**Manganese-zinc ferrite** (Mn Zn, with the formula $\text{Mn}_a\text{Zn}_{(1-a)}\text{Fe}_2\text{O}_4$). Mn Zn has higher permeability and saturation induction than Ni Zn).

**Nickel-zinc ferrite** (Ni Zn with the formula $\text{Ni}_a\text{Zn}_{(1-a)}\text{Fe}_2\text{O}_4$): Ni Zn ferrite exhibits higher resistivity as compared to that of Mn Zn, and are therefore, more suitable for frequency above 1 MHz.

For applications below 5 MHz, Mn Zn ferrites are used; above that, Ni Zn is the usual choice. The exception is with common mode inductors, where the threshold of choice is at 70 MHz.

**1.7.2 Hard ferrites**

In contrast, permanent ferrite magnets are made of hard ferrites, which have a high coercivity and high remanence after magnetization. Iron oxide and barium or strontium carbonate are used in manufacturing of hard ferrite magnets. The high coercivity means the materials are very resistant to becoming demagnetized, an essential characteristic for a permanent magnet. They also have high magnetic permeability. These so-called ceramic magnets are cheap, and are widely used in household products such as refrigerator magnets. The maximum magnetic field $B$ is about 0.35 tesla and the magnetic field strength $H$ is about 30 to 160 kilo-ampere turns per meter (400 to 2000 oersted). The density of ferrite magnets is about 5 g/cm$^3$. The most common hard ferrites are:

**Strontium ferrite**, $\text{SrFe}_{12}\text{O}_{19}$ (SrO·6Fe$_2$O$_3$): It is used in small electric motors, micro-wave devices, recording media, magneto-optic media, telecommunication and electronic industry.

**Barium ferrite**, $\text{BaFe}_{12}\text{O}_{19}$ (BaO·6Fe$_2$O$_3$): It is a common material for permanent magnet applications. Barium ferrites are robust ceramics that are generally stable to moisture and corrosion-resistant. They are used in e.g. loudspeaker magnets and as a medium for magnetic recording, e.g. on magnetic stripe cards.

**Cobalt ferrite**, $\text{CoFe}_2\text{O}_4$ (CoO·Fe$_2$O$_3$): It is used in some media for magnetic recording.
1.8 Ferroelastic materials

Ferroelastic materials develop a spontaneous strain below a phase transition temperature. From the symmetry point of view, the material undergoes a structural phase transition from a high symmetry phase to a low symmetry phase, which is characterized by a ‘broken symmetry’ of the high symmetry phase.

It is a phenomenon in which a material may exhibit a spontaneous strain. In ferroics, ferroelasticity is the mechanical equivalent of ferroelectricity and ferromagnetism. When stress is applied to a ferroelastic material, phase change will occur in the material from one phase to an equally stable phase, either of different crystal structure (e.g. cubic to tetragonal), or of different orientation (a 'twin' phase). This stress-induced phase change results in a spontaneous strain in the material.

1.9 Multiferroics

Multiferroic materials are materials that exhibit at least two, and sometimes all three, types of ferroic ordering in the same phase. The ferroic orderings are ferroelectric, ferromagnetic and ferroelastic and relate to the type of applied field required for the material to exhibit a spontaneously polarized state. Fig.1.6 shows these types of ferroic ordering, where an applied electric, magnetic or stress field induces a spontaneous electric polarization, magnetization or strain, respectively. However, in multiferroics additional levels of ordering can result from the coupling between the different types of ferroic ordering. For instance, in a magnetoelectric multiferroic an applied magnetic field can be used to control the polarization, or an applied electric field could be used to control the magnetization.

In a multiferroic, the coexistence of at least two ferroic forms leads to additional interactions. For example, in a magnetoelectric multiferroic, a magnetic field may control $P$ or an electric field may control $M$ [23]. If the coupling between electric and magnetic order parameters exists, a multiferroic material becomes a magnetoelectric material. But a magnetoelectric (or a multiferroic) material does not necessary to be a multiferroic (or a magnetoelectric) material as shown in Fig. 1.7.
Fig. 1.6 Ferroic ordering, the electric field $E$, magnetic field $H$, and stress $\sigma$, lead to a spontaneous electric polarization $P$, magnetization $M$, and strain $\varepsilon$ respectively.

Fig. 1.7: Intersection of the subsets representing multiferroics [24].

Generally, ferroelectrics and/or ferromagnetic are considered to be a subset of electrically and/or magnetically polarizable materials, such as paraelectric and antiferroelectric, paramagnetic and antiferromagnetic.

Two types of single-phase multiferroics exist in the materials; type I (ferroelectric and magnetic orders originating from independent phenomena) and type II (ferroelectricity directly linked to the magnetic order). In type I multiferroic material, the ferroelectricity and magnetism are originated from different sources and appear largely independently of one another, though some coupling exist between them. In this type of materials, ferroelectricity
typically appears at higher temperatures than magnetism, and the spontaneous polarization $P_s$ is often rather large in some of the multiferroic such as bismuth ferrite (BiFeO$_3$), bismuth manganite (BiMnO$_3$) and yttrium manganite (YMnO$_3$). This also leads to the weak coupling between the ferroic states. BiFeO$_3$ is a commonly known as type I single phase multiferroic. Zhao et al. [25] demonstrated electric-field-control of antiferromagnetic domains in BiFeO$_3$ through coupling of antiferromagnetic and ferroelectric domains to the underlying ferroelastic domain structure. In type II multiferroics (i.e., TbMnO$_3$, Ca$_3$CoMnO$_6$) ferroelectricity occurs only in the magnetically ordered state, implying a strong coupling between the two. However, the polarization in this type of materials is usually much smaller. In both cases, magnetic interactions give rise to a net polarization at low temperatures, which directly couples the ferroic order parameters [26-27]. The coupling between the ferroic order parameters has been largely limited to magnetic field control of ferroelectric polarization [28]. The conditions for the occurrence of ferroelectricity and magnetic order in the same material is often accompanied by ferroelasticity, which implies (a) the presence of adequate structural building blocks permitting ferroelectric-type ionic movements, (b) magnetic-interaction pathways, usually of the super exchange type, and (c) the fulfillment of symmetry conditions [29]. Magnetoelastic (ME) coupling describes the influence of a magnetic (electric) field on the polarization (magnetization) of a material.

Landau and Lifshitz [30-31], free energy ($F$) in terms of the electric field $E$ and magnetic field $H$ is expressed as

$$F(E, H) = F_0 - P_s E_i + M_s H_i - \frac{1}{2} \varepsilon_{ij} E_i E_j - \frac{1}{2} \mu_{ij} H_i H_j - a_{ij} E_i H_j - \frac{1}{2} \beta_{ijk} H_i E_j E_k - \frac{1}{2} \gamma_{ijk} E_i H_j E_k$$

(1.1)

Here, $i$, $j$ and $k$ are directions, $P_s$ and $M_s$ are the spontaneous polarization and magnetization, $\varepsilon$ and $\mu$ are the electric permittivity and magnetic permeability and $a$ expresses the linear magneto-electric coupling, $\beta$ and $\gamma$ express bilinear magneto-electric coupling. Electric polarization and magnetization are obtained by taking derivative with respect to electric and magnetic field.

$$P_i(E, H) = -\partial F/\partial E_i = P_{si} E_i + \varepsilon_{ij} E_j + a_{ij} H_j + \frac{1}{2} \beta_{ijk} H_j E_k + \cdots$$

(1.2)

$$M_i(E, H) = -\partial F/\partial H_i = M_{si} + \mu_{ij} H_j + a_{ij} E_j + \frac{1}{2} \gamma_{ijk} E_j E_k + \cdots$$

(1.3)
In formula (1.2) setting $P_s = 0$, $E_i = 0$, one obtains

$$P_i(H) = \alpha_{ij}H_j + \frac{1}{2} \beta_{ijk}H_jH_k + \ldots$$  \hspace{0.5cm} (1.4)

In formula (1.3) setting $M_{si} = 0$, $H_i = 0$, one obtains

$$M_i(E) = \alpha_{ij}E_i + \frac{1}{2} \gamma_{ijk}E_jE_k + \ldots$$  \hspace{0.5cm} (1.5)

In the electric polarization equation, $P_s$ is spontaneous polarization. In the third term $\alpha_{ij}$, called the linear magnetoelectric coefficient, plays an important role in magnetoelectric phenomena.

Equations (1.4) and (1.5) express the magnetic (electric) induced polarization (magnetization). The boundary condition of linear ME coupling was discussed by W. F. Brown [31]. The coupling coefficient was expressed by:

$$\alpha_{ij} = \sqrt{\varepsilon_0 \mu_0 \varepsilon_{ij} \mu_{ij}} = \sqrt{\varepsilon_{ij} \mu_{ij}}/c_0$$  \hspace{0.5cm} (1.6)

The formula highlights that large linear ME coupling can be written by large electric permittivity and magnetic permeability even without ferroic orders. For the magnetoelectric coefficient to be non-zero, simultaneous violation of space inversion symmetry and time reversal symmetry is essentially required, i.e. multiferroic possessing both ferroelectric and ferromagnetic properties are required.

In composite materials, the ME effect is realized by using the concept of product properties introduced by Van Suchetelene. The ME effect can also be realized by coupling the thermal interaction in pyro-electric–pyro-magnetic composites.

**Some basic requirements of a multiferroic material are enumerated as follows:**

- **Symmetry.**

Ferroelectricity requires the condition of non-centro symmetry and allows an electric polarization. Out of 31 point groups; 13 point groups (1, 2, 2', m, m', 3, 3m', 4, 4m'm', m'm2', m'm2', 6, and 6m'm') are found in both magnetic and electric states, allowing both properties to exist in the same phase.
Introduction

❖ **Electrical Properties**

A ferroelectric material must be an insulator; otherwise, an applied electric field would induce an electric current to flow, rather than causing an electrical polarization. Ferromagnets, although not required to have specific electrical properties, are often metals. Of course, there exist few antiferromagnetic, ferromagnetic and ferroelectrics which are usually insulating materials.

❖ **d⁰ electrons**

The ferroelectric materials with perovskite structure require a formal charge corresponding to the d⁰ electron configuration on the B-site cation. Hence, if there are no d electrons to create localized magnetic moments, then there can be no magnetic ordering of any type (i.e., ferro-, ferri-, or antiferromagnetic).

❖ **Lone pair multiferroic**

For the coexistence of magnetism and ferroelectricity in multiferroics, one possible mechanism is the lone pair driven mechanism [16], where the A-site (i.e., Bi-site) drives the displacement to occur ferroelectricity and partially filled d shell on the B-site (i.e., Fe/Mn) contributes to the magnetism in BiFeO₃, BiMnO₃ [32] etc. The Bi³⁺ ion has a stereo-chemically active 6s² lone pair electron, which displaces this ion from the centro-symmetric position with respect to the coordinated oxygen ions. Then, the A-site Bi ion is responsible for ferroelectricity and the B-site Fe/Mn ion is responsible for the magnetism in a single phase of the above compounds.

1.10 Types of multiferroics

The types of multiferroics are presented below:

1.10.1 Single phase multiferroic

To find the single-phase multiferroic materials we should consider the specific criteria for ferromagnetism and ferroelectricity as mentioned above. Ferroelectric materials must be electrically insulator and have a noncentro-symmetric unit cell. Ferromagnetic materials tend to be metals; however, we can look to ferrimagnetic oxides to satisfy the insulating
requirement. Initially the perovskite structure seems a likely candidate for a single phase multiferroic material, due to the existence of both ferroelectric (ATiO$_3$, A=Ba, Pb, Sr) and magnetic (LaMnO$_3$, GdFeO$_3$) compounds with this structure. In order to make a magnetic ferroelectric one might suggest replacing the $d^0$ Ti cation with a magnetic cation with $d$ electrons. However, once $d$ electrons are added to adopt a noncentro-symmetric unit cell, distortion is lost. Placing a magnetic cation with $d$ electrons on the B site of an ABO$_3$ perovskite prevents ferroelectric behavior; therefore, we must look towards different approaches in finding a single-phase multiferroic material. One method is to synthesize a material where the electronic dipole moment and the magnetic moment come from different atoms within the unit cell. This has been accomplished in a limited number of Bi- based perovskite multiferroics, taking advantage of the lone-pair effect of the large Bi cation to provide the ferroelectric behavior, while a small magnetic cation is placed at the B site (B = Fe, Mn). Other approaches have included double perovskite systems, where one sublattice contains magnetic ions on the B- site replacing the $d^0$ cations. However, these approaches tend to have low ferroelectric and magnetic ordering temperatures, as a result of the dilution of the sub-lattices [33-34]. Other candidate multiferroic materials include geometrically driven ferroelectrics, for example the hexagonal perovskite YMnO$_3$. In the case of YMnO$_3$ the relative sizes of the A and B cations make the cubic perovskite phase unfavorable, and geometry drives the distortion to a lower symmetry ferroelectric phase [35]. Efforts have been made to design to develop room temperature single phase multiferroics and switchable order parameters in oxides [35a]. Kimura et al. have found that spin frustrated magnetic systems are also candidate multiferroic materials. They found that the spin frustration in the TbMnO$_3$ system leads to a sinusoidal magnetic ordering that causes a magneto-elastically induced lattice modulation and hence a polarization [26]. In other words, the spin frustration allows for a noncentro-symmetric structure, thereby fulfilling the ferroelectric symmetry requirement. The single-phase multiferroics outlined above. What stands out is that of these materials only BiMnO$_3$ has ferromagnetic ordering, and BiFeO$_3$ is the only material that has both a magnetic and a ferroelectric ordering temperature above room temperature. BiFeO$_3$(BFO) is also promising due to the high saturation polarization reported for this compound [36]. Beside BFO there are other materials in single phase found to have superior properties such as Pb(Fe,M)$_x$(Zr,Ti)$_{1-x}$O$_3$ [M=Ta,Nb], where the magneto-electric constants ($\alpha_{ME}$) increases supralinearly with Fe concentrations and found to be superior over BFO in
device application as their dielectric loss is very low [36a]. The room temperature magnetic switching of ferroelectric domains found in single phase multiferroic PZTFT with good coupling constant [36b] has promising application. Tilt engineering of ferroelectric and ferromagnetic polarization in the layered perovskite (Ca$_x$Sr$_{1-x}$)$_{1.15}$Tb$_{1.85}$Fe$_2$O$_7$ which change its symmetry and simultaneously generates electrical polarization [36c] and magnetization above room temperature and magnetically-induced switching of polarization order parameters observed in Aurivillius phase thin films [36d]. Although, these materials are proof that magnetic and ferroelectric ordering can coexist in a single phase, they are characterized by low ordering temperatures and low saturation polarizations, causing their usefulness in actual device applications to be limited.

### 1.10.2 Multi-phase multiferroics

To overcome the limitations of single-phase multiferroics let us examine developments in composite or multi-phase multiferroic materials. Composite multiferroics typically consist of alternating layers of piezoelectric and magnetostrictive materials. Piezoelectric and magnetostrictive materials undergo a shape change in an applied electric or magnetic field, respectively. The coupling in these materials is mechanical in nature. Because neither the piezoelectric or magnetostrictive material alone has magnetoelectric properties, the magnetoelectric response is referred to as a product property [37]. When a magnetic field is applied the magnetostrictive material is strained, this strain induces a stress on the piezoelectric material, which in turn generates a polarization, and an electric field, in the piezoelectric phase. Typical materials used in these composites are Terfenol-D, TbDyFe$_2$, a giant magnetostrictive alloy and lead zirconate titanate (PZT) [38]. These materials are made by stacking them one on top of another and bonding with a conducting compound, such as silver epoxy. The figure of merit for these materials is the magneto-electric coefficient, $\alpha_E$, which is calculated by measuring the change in electric field, $\delta E$, generated by applying an ac magnetic field, $\delta H$, to a biased sample

$$\alpha_E = \frac{\delta E}{\delta H} \quad \text{(1.7)}$$

Although these multilayer systems have high theoretically predicted values for $\alpha_E$, actual experimental values tend to be much lower [39]. One reason is that these are not true bilayer
systems, because the layers are joined by silver epoxy them in fact have 3 layers. These additional interfaces, piezoelectric/silver epoxy and silver epoxy/magnetostrictive material, lead to poor mechanical coupling between the piezoelectric and magnetostrictive layers. In order to enhance interface coupling, researchers looked towards composites with good lattice matching. Due to their comparable lattice dimensions one example of a prime candidate material would be a composite where the magnetic component has the spinel structure, as seen in ferrites, while the piezoelectric component has the perovskite structure, PZT [40]. These materials are prepared by laminating stacked tape cast films of piezoelectric and mangetostrictive materials under high pressure and temperature [41]. Particulate multiferroic composites have also been prepared with micron sized particles of BaTiO$_3$ and MFe$_2$O$_4$ (M=Ni, Co, Mn) [42], revealing an increase in the magneto-electric coefficient with decreasing particle diameter.

However, these multiferroics are still plagued with problems. Although PZT/Ferrite and BaTiO$_3$/Ferrite composites have good lattice matching, they have a large thermal expansion mismatch, which leads to cracks forming at the interface upon firing. These interfacial cracks inhibit the ability to get good coupling between the phases. Other likely causes for the low values of $\alpha_E$ are leakage current through the low resistivity ferrite phase, any impurity phases that are present, and porosity. In this dissertation new composite materials will be developed to overcome the limitations of these materials, and to work towards creating a multiferroic with superior properties.

1.11 Problems with the Non-Polymeric ME materials

The magnitude of the ME coupling coefficient in most of the single phase MF materials is in the range of 1–20 mV/(cm Oe) which is considered insufficient for most of the proposed practical applications [29]. In addition, there is a wide variation of the transition temperatures (paraelectric to ferroelectric, paramagnetic to antiferromagnetic, antiferromagnetic to ferromagnetic) for the single-phase ME materials and a limited number of materials that exhibits ME behavior at room temperature [43]. In this way, most of these MEs can be only used at low temperatures ($\approx 10$ K), which severely hinders the design and applications of devices.
Despite ME coefficients obtained in ceramic MF composites being three orders of magnitude higher than in single phase materials [44], such composites may become fragile and are limited by deleterious reactions at the interface regions, leading to low electrical resistivity and high dielectric losses $> 0.1$, hindering in this way the incorporation into devices [45]. Apart from the aforementioned disadvantages, ceramic composites still have other problems such as being expensive, dense and brittle, which can lead to failure during operation. [46-47]. In this way, ceramic-based ME materials are not attractive from a technological point of view.

### 1.12 Polymer based magnetoelectric materials

A more recent approach to obtain highly flexible and non-brittle ME composites and to solve all the aforementioned problems is to use polymer-based nanocomposites [48-49]. In comparison with the ceramic ME composites, polymer-based ME materials can be easily fabricated by conventional low temperature processing into a variety of forms, such as thin sheets or molded shapes, and can exhibit improved mechanical properties [48]. There are three main types of magnetoelectric polymer-based composites can be found i.e., (i) nanocomposites, (ii) polymer as a binder, and (iii) laminated composites. So far, three main types of bulk ME composite have been investigated both experimentally and theoretically (a) magnetic metals/alloys e.g. laminated Terfenol-D and Metglass and piezoelectric ceramics; (b) laminated Terfenol-D and Metglass and piezoelectric polymers; and (c) particulate composite of ferrite and piezoelectric ceramics, e.g. lead zirconate titanate [50].

Here we will concentrate regarding the synthesis and characterization of multiferroic polymer nanocomposite with the introduction of magnetic ferrite nano particle (within the range of 20nm) in the PVDF (poly vinylidene fluoride, organic ferroelectric) matrix.

### 1.13 Spinel ferrite nanoparticles

Recently, the synthesis of magnetic materials on the nanoscale has been a field of intense study, due to the novel mesoscopic properties shown by particles of quantum dimensions located in the transition region between atoms and bulk solids [51]. Quantum size effects and the large surface area of magnetic nanoparticles dramatically change some of the magnetic properties and exhibits super paramagnetic phenomena and quantum tunneling of
magnetization, because each particle can be considered as a single magnetic domain. Magnetic nanoparticles of spinel ferrites are of great interest in fundamental science, especially for addressing the fundamental relationships between magnetic properties and their crystal chemistry and structure. Spinel ferrites have been investigated in recent years for their useful electrical and magnetic properties and application information storage system, magnetic bulk cores, magnetic fluids, microwave absorbers and medical diagnostics. The synthesis and magnetic structure characterization of spinel metastable nanoferrites have been investigated with much interest [52-53] and a lot of attention has been focused on the preparation and characterization super paramagnetic metal oxide nanoparticles of spinel ferrites, $\text{MeFe}_2\text{O}_4$ (metal Me = Co, Mg, Zn, etc.) [54-55]. The rich crystal chemistry in spinel ferrite systems offers excellent opportunities for understanding and fine-tuning the superparamagnetic properties of nanoparticles by chemical manipulation.

### 1.13.1 Structure of Spinel ferrite

The spinel ferrites structure $\text{MeFe}_2\text{O}_4$, where Me refer to the divalent metal, and can be described as a cubic close-packed arrangement of oxygen atoms, with $\text{Me}^{2+}$ and $\text{Fe}^{3+}$ at two different crystallographic sites. These sites have tetrahedral and octahedral oxygen coordination (termed as A and B-sites, respectively), so the resulting local symmetries of both sites are different (fig 1.8).

![fig 1.8](image1.png)

**Fig.1.8 The Structure of Spinal ferrite**

The spinel structure contains two cation sites for metal cation occupancy. There are 8 A-sites in which the metal cations are tetrahedrally coordinated with oxygen, and 16 B-sites
which possess the octahedral coordination. When the A-sites are occupied by $Me^{2+}$ cations and the B-sites are occupied by $Fe^{3+}$ cations, the ferrite is called a normal spinel. If the A-sites are completely occupied by $Fe^{3+}$ cations and B-sites are randomly occupied by $Me^{2+}$ and $Fe^{3+}$ cations, the structure is referred to as an inverse spinel. In most spinels, the cation distribution possesses fraction of the $Me^{2+}$ and $Fe^{3+}$ cations. Magnetically, spinel ferrites display ferromagnetic ordering. The magnetic moments of cations in the A and B-sites are aligned parallel with respect to one another. Between the A and B-sites the arrangement is antiparallel and as there twice as many B-sites as A-sites, there is a net moment of spins yielding ferrimagnetic ordering for the crystal. The choice of metal cation and the distribution of ions between the A and B-sites, therefore offer a tunable magnetic system [56]. According to the distribution of cations, there are the following types of ferrospinels:

(1) Normal spinel structure, where all $Me^{2+}$ ions occupy A-sites; structural formula of such ferrites is $Me^{2+}[Fe^{3+}_2]O_4^{2-}$. This type of distribution takes place in zinc ferrites $Zn^{2+}[Fe^{2+}Fe^{3+}]O_4^{2-}$.

(2) Inverse spinel structure, where all $Me^{2+}$ are in B-positions and $Fe^{3+}$ ions are equally distributed between A and B-sites: structure of these ferrites are $Fe^{3+}[Me^{2+}Fe^{3+}]O_4^{2-}$. Magnetite $Fe_3O_4$, ferrites $NiFe_2O_4$, and $CoFe_2O_4$ have an inverse spinel structure.

(3) Mixed spinel structure, when cations $Me^{2+}$ and $Fe^{3+}$ occupy both A and B-positions; structural formula of the ferrite is $Me_{1-2\delta}^{2+}Fe\delta^{3+}[Me_{\delta}^{2+}Fe2 - \delta^{3+}]O_4^{2-}$. Where $\delta$ is the degree of inversion. $MnFe_2O_4$ represents this type of structure and has an inversion degree of $\delta = 0.2$ and its structural formula therefore is $Mn_{0.8}^{2+}Fe_{0.2}^{3+}[Mn_{0.2}^{2+}Fe_{1.8}^{3+}]O_4^{2-}$. Mn-Zn ferrites ferrites also have a mixed spinel structure ($Zn^{2+}$ prefers to occupy A-sites)$Zn\delta^{2+}Mn_{1-x-y}^{2+}Fe_{1-x-y}^{3+}[Mn_{1-x-y}^{2+}Fe_{1+x+y}^{3+}]O_4^{2-}$, where $\delta = 1 - x - y$.

Magnetic properties of ferrites have been explained by Neel [57], who postulated that the magnetic moments of ferrites are a sum of magnetic moments of individual sublattices. In the ferrospinels these are: sublattice A consisting of cations in tetrahedral position and sublattices B with cations in octahedral positions. Exchange interaction between electrons of ions in these sub-lattices have different value. Usually the interaction between magnetic ions of sub-lattices A and B (A-B interaction) is the strongest. A-A interaction is almost ten
times weaker and B-B interaction is the weakest. The dominant A-B interaction leads to complete or partial (non-compensated) anti ferromagnetism (ferrimagnetism) [57].

In the inversed ferrites one half of Fe$^{3+}$ is placed in A-sites and another half in B-sites. Their magnetic moments are mutually compensated and the resulting moments of the ferrite, are due to the magnetic moments of bivalent cations Me$^{2+}$ in B-positions (Fig 1.9 a). Due to this, magnetic moments of a part of Fe$^{3+}$ ions (which are now only in B-position) becomes reversibly oriented which leads to the decrease of the total magnetic moment in ferrites. Higher the temperature, greater is the relative effect of the A-B exchange weakening due to the thermal fluctuation, resulting in decreased magnetization[58].

![Cation distribution in spinel ferrites](image)

**Fig. 1.9** Cation distribution in spinel ferrites: (a) inverted ferrites, (b) manganese ferrites

### 1.14 Polyvinylidene fluoride (PVDF)

The research activity on electro-active organic polymer has been focused mainly on three aspects: dielectric–ferroelectric, electrically conductive, and nonlinear optical properties. Pyroelectric, piezoelectric and ferroelectric phenomena in inorganic and organic molecular material have been studied for quite some time. Kocharyan in 1963 first reported on piezoelectricity for two organic polymer, poly (methyl methacrylate) and poly(vinyl chloride). Few example Nylon 11, polylactic acid, polyvinylidene Fluoride (PVDF) polymers exhibits piezo-, pyro- and ferroelectricity. But PVDF has gained special attention in the form of polymer matrix because of its versatile application in the industrial field owe to its high dielectric constant, low loss, high thermal stability, chemical resistance, light weight and low density [59-60]. In 1969 Kawai first demonstrated significant enhancement in the piezoelectric properties of poly (vinylidene fluoride) by electrets formation [61]. In 1971, the ferroelectric properties of poly (vinylidene fluoride) were discovered [62]. PVDF and its co-polymer find application in electromechanical system and charge storage capacitors [63-64].
PVDF is a semi-crystalline polymer which is 50% amorphous. The structure of monomer of this polymer is \(-\text{CH}_2\text{-CF}_2\)- and the chain occurs mainly in head to tail configuration. The molecular weight of PVDF is in the range of 60-70 kg/mol [65]. It has a complex structure and depending upon the chain conformation as T (trans) and G (gauche) linkages it has five distinct crystalline phases: non-polar α-phase and ε-phase, as well as polar β-phase, γ-phase and δ-phase [64]. This crystalline phase can be transformed into each other under specific conditions. Among all the phases, α and β are the most common and melt processing commonly results in the non-polar α-phase. These two phases have gained most interest because α-phase is thermodynamically stable at room temperature and pressure and β-phase is kinetically stable under these condition and exhibit excellent piezoelectric, pyroelectric and ferroelectric properties [64]. The β-phase of PVDF can be obtained from α-phase PVDF by mechanical stretching with a temperature between 70-100°C and a stretch ratio of \((L_{\text{final}}/L_{\text{initial}})\) in the range of 3-5 [66].

The α-phase of PVDF’s occurs in trans-gauche-trans-gauche-(TGTG) formation. The structure is neither helical (planar) nor zig-zag but a combination of two. The β-phase of PVDF forms a zig-zag of TT bond that remains in the same plane as the carbon backbone which results in most polar phase among other. PVDF crystals are mainly formed in β-phase due to the transformation of α- to β- crystal induced by the stretching force.

![Structure of α-PVDF (left) and β-PVDF (right) [67]](image-url)
1.15 Nanomaterial

Nanostructured materials have become increasingly popular of the ages because of the possibility of enhanced properties and the capability of property tailoring. In application point of view, every area has the demand of smaller, faster, lighter, efficient, portable and durable device. We need smaller, lighter and longer lasting appliances which are lightweight, fuel efficient and have advanced features. All the above features have drawn considerable attention towards nanotechnology. Properties and behavior of materials at these ‘nano’ levels can vary differently when compared with their bulk counterpart. Thus, an understanding of nanostructure i.e., the structure and properties of materials at nanoscale (scale length within 1-100nm) has drawn a considerable attention. Thus “nanotechnology’ is used to describe the physical, chemical, and biological phenomena occurring at nanoscale. The huge charm of nanomaterials is that their properties are different from, and mostly superior to, those of conventional materials that have a phase or grain structure on a coarse grain size structure. Many properties of the solids depend on the size range over which they are measured. Nanomaterial research was investigated by the possibility of utilizing the increased surface area to volume ratio in applications requiring surface chemical activity for uses catalyst and pigment [68]. In addition to the betterment of chemical properties, it has been recognized that the reduction of microstructural length scale to nanometer range could result in a modest improvement in the physical and mechanical properties of materials. A reduction of powder particle size to nanometric dimensions result in a considerable increase in surface area, aiding in faster mass transport during sintering (Herring’s scaling law) [69]. Nanostructured materials are also one of the best growing research areas in the field of material science. They can be in the form of amorphous, crystalline or mesoporous materials according to the distributions of atoms and size of the pores [70-73]. When nanomaterial is in the crystalline form they are called nanocrystalline material [74]. Physics of such nanoscale materials is different from the macroscale properties of the same substance. The difference in properties, which are often superior, arises due to; (i) large surface to volume ratio, (ii) high hardness, (iii) high compressive strength, (iv) high electric modulus(v) high dielectric constant etc. [75].
1.15.1 Classification of nanomaterials

The term nanomaterials’ encompassed a wide variety of technologically important materials. Hence, for convenience, it is essential to subdivide them into various groups based either on their dimensions or microstructures. Based on physical dimensions i.e., dimensionality factor (D), [76] nanostructured materials (NSM) may be classified [77-78] into four types.

If one dimension of a bulk nanostructure (3-D) is reduced to the nano-range while the two other dimensions remain bulk, then the structure is known as nano-well (2-D). If two dimension are so reduced and one remains large, then they obtained structure is known as nano-wire(1-D) and the extreme case of this process of size reduction in which all three dimension reach the low nanometer range, it is called nanosized clusters(0-D) or quantum dots.

In general, nanocrystallites exhibits size dependent properties such as higher energy band gaps, lower melting points and deviation in associated thermodynamic features [79-80]. The origin of these changes lies in the modification of surface structure and related microstructure. The properties of nanocrystalline material deviate from those of bulk single crystal, polycrystals, or bulk glasses on the same composition. This deviation results from the reduced size and dimensionality of such small crystallites as well as from the numerous interfaces between adjacent crystallites.

1.16 Thermodynamics of Nano-crystalline materials

There are usually two processes for formation of nanocrystals, first is the formation of very small particles or nuclei of the new phase (nucleation) that are capable of growing. The other growth presents a situation in which the nuclei increase in size, and the process some volume of the parent phase disappears [81]. In homogenous nucleation, the probability of nucleation occurring at any given state is identical to that of any other size within the volume of the parent phase. If $\Delta f$ is the free energy change accompanying the formation of a spherical new phase, then it can be written as

$$\Delta f = \frac{4}{3} \pi r^3 \cdot \Delta g + 4 \pi r^2 \gamma$$  \hspace{1cm} (1.8)
Where \( r \) is the radius of the particle, \( \Delta g \) is the change per unit volume in Gibbs free energy and \( \gamma \) is the surface energy per unit area of the interface separating the parent and the product phase. By setting \((d\Delta f/dr)\) equal to zero, the critical radius \((\hat{r})\) for the stable existence of the particle can be found. The \( \hat{r} \) is given by \( \hat{r} = -\frac{2\gamma}{\Delta g} \). The stable \( r \geq \hat{r} \) particles which can grow in size, independently called nuclei, while the unstable particles \( r < \hat{r} \) particles (macroscopic domains) are called embryos [15].

1.17 Synthesis of nanomaterials

Materials formed, entirely or partially, by crystals of nanometer size are not in stable equilibrium. Rather, they retain a consistent amount of excess free energy [76, 82-83]. This parameter determines the stability as well as the feasibility of the formation of a new system. The two categories can be singled out: materials in unstable equilibrium and materials in meta-stable equilibrium. Among the former are the crystalline materials prepared by vapor condensation or ball milling. The latter pertains to the materials containing a nanocrystalline phase produced by solidification to cause controlled nucleation of crystals. In general, there are two distinct approaches to obtain nanocrystalline materials: (i) Top down method (physical method) and (ii) bottom-up method (chemical method).

In the top-down process, the initial bulk materials break into pieces by the application of some mechanical energy and get stabilized in their nanometer range [84].

Ball milling is an efficient tool for grinding different kind of materials into fine powder processing of brittle materials like ceramic results in extremely fine powders which show excellent properties as pigments or can be used as a raw material for manufacturing of advanced ceramics [85]. The large surface area results in high sintering activity and permits full densification at comparatively low temperatures. Additionally, the produced components show superior mechanical properties due to the nanosized grain structure.

1.18 Applications of nano-materials

Based on the arrangement, conventional materials can be classified as crystalline and amorphous materials which differ from each other in that the former has both short and long range order while the latter has only short range order. Nanocrystalline materials consist of
a crystalline component by all crystal atoms and a boundary component by boundary atom. They exhibit modified atomic arrangement in their lattice structure. Due to the unique atomic arrangements nanocrystalline materials have the potential to produce novel material properties. The short range disorder in the interface influences thermodynamics, magnetic, electrical properties and the small grain size affect the sintering, plasticity and diffusivity. Nanomaterials have many improved properties as compared to coarse-grained conventional materials and metallic materials. Since nanomaterials possess unique physical, chemical and mechanical properties, they can be used for a wide variety of applications.

It is a well known fact that there is a lower diffusion activation energy of atoms in nanocrystals or nanostructured materials, thus larger diffusion coefficient than the corresponding bulk counterpart due to the increase of surface (interface) /volume ratio of the nanocrystals or nanostructured materials [86-87]. The potential of this phenomenon for industrial application is an evident drop of temperature for any diffusion process.

In recent years great interest has also been evoked on a variety of nanostructured ferroelectric materials. The uses of capacitors constructed from ferroelectric thin films have simulated interest in developing ferroelectric non-volatile memory devices [88]. It is difficult to realize a noncrystalline feature by the conventional process, as high temperature calcinations always leads to coarsening and aggregation of fine ceramic particles. In a fundamentally different approach, phase formation in ball-milled samples is realized at comparatively very low temperature, depending on the specific ceramic material concerned.

1.19 Literature review and selection of materials

Magnetic ceramics may be divided into one of three different classes; spinel ferrites, hexagonal ferrites and the rare earth ferrites (garnet materials). The soft ferrites crystallize in the spinel structure, the structure of which was derived from the mineral spinel (MgOAl₂O₃ or MgAl₂O₄) [22, 89]. Fine magnetic particle systems have received a growing and renewed interest in the last few years in the wide possibilities of applications in the nanostructured materials technology. Nanosized magnetic particles have properties, which are drastically different from those of the corresponding bulk materials. This results from reduced sizes and effects of magnetic interactions between particles. Because of the large specific area, surface
Introduction

Ferromagnetism of metal elements such as Ni, Co, Mn or Zn is derived from the unpaired electron spins in their atoms. The highest magnetic moments and therefore the highest saturation magnetizations are to be found in the metals themselves. Ferrimagnetic ferrites, based on metal oxides suffer from a dilution effect of the large oxygen ions in the crystal lattice [90]. The oxygen ions also serve to insulate the metal ions and therefore greatly increase the resistivity, making the ferrite especially useful at higher frequencies. The nano scale spinel ferrite has a face-centered cubic (FCC) structure of the form $\text{MFe}_2\text{O}_4$, where M is a divalent atom. The structure contains two interstitial sites occupied by metal cations, namely tetrahedral (A) site and octahedral (B) site. This produces a different local symmetry. The cationic distribution in octahedral and tetrahedral sites is characterized by the inversion parameter $\gamma$ defined as the fraction of divalent ions in the octahedral sites. The net magnetization, being proportional to the difference between A and B sub lattice magnetization, depends on the cationic distribution. In the same manner, since single-ion anisotropy of a specified ion depends on the interstitial site, magnetic anisotropy also depends on the inversion degree. Moreover, several techniques have been used to study the spin-canting phenomenon such as neutron diffraction and $^{57}\text{Fe}$ Mossbauer [91]. The results provided evidence that spin canting can be either restricted to a single or extended to both cationic sites.

1.19.1 Nickel ferrite ($\text{NiFe}_2\text{O}_4$)

Nickel ferrite is a typical soft ferrimagnetic material, which crystallizes in a completely inverse spinel type with all nickel ions located in octahedral sites and iron ions occupying tetrahedral and octahedral sites. Several studies have been devoted to the synthesis and the magnetic properties of $\text{NiFe}_2\text{O}_4$ nanoparticles prepared by a great variety of chemical routes. Previous report reveals that the magnetic behavior of these nanoparticles depends mainly on the synthesis route. The most common characteristic is their super paramagnetic
behavior and the reduction of the saturation magnetization in comparison with the corresponding bulk material (55 emu g\(^{-1}\)) [92-93]. Ferrimagnetisms in the material originates from the magnetic moment of anti-parallel spins between Fe\(^{3+}\) ions at tetrahedral sites and Ni\(^{2+}\) ions at octahedral sites. This ferrite has many industrial applications including biomedical [94]. Though this material has a small value of magnetic coercivity, it is chemically stable and mechanically hard with good electrochemical performance [95]. In Mixed spinel ferrite NiFe\(_2\)O\(_4\) the Fe\(^{3+}\) spins have a canted structure and the canting angle increases with grain-size reduction. It is possible that the core Fe\(^{3+}\) spins are also canted because of the magnetocrystalline anisotropy introduced by the occupancy of the Ni\(^{2+}\) ions in the tetrahedral sites of ball milled sample [96]. NiFe\(_2\)O\(_4\) (NFO) also has been identified as a negative electrode material for Li-ion battery [97] and super capacitor [98]. It is now a well-established fact that the particle/grain size and shape play an important role for tailoring of electrical, magnetic and electrochemical properties of materials for device applications [99-100]. Therefore, the selection of suitable synthesis/fabrication and characterization methods is highly desirable to get micro- and nano-structures and particles [101]. Besides this, nickel ferrite, as a semiconductor, has attracted much attention of researchers to develop nano-powder and structure of the material for technological applications. Above properties are not only dependent on particle size, but also on various other factors such as chemical composition, preparation technique, stoichiometry, sintering time, temperature and atmosphere, substitution of different ions, etc., [102]. Because of strong dipole–dipole interaction, there are some problems and challenges associated with utilization of nano-crystalline magnetic materials for devices. One of them is an aggregation of nano-particles due to the large surface reactivity [103]. Other than this, the nano-fabrication lowers the coordination between atoms on the surfaces, which causes the reduction in magnetic moment as compared to the bulk structures [104]. The primary ferrite nano-particles rapidly aggregate to form spherical clusters in order to minimize their surface energies.

1.19.2 Cobalt Ferrite (CoFe\(_2\)O\(_4\))

Cobalt ferrite was rarely considered as a permanent magnet material mainly because of its low coercivity [105]. However, nano-crystalline cobalt ferrite thin films grown on (100) MgO substrate using pulsed laser deposition technique found to be a hard magnetic material.
due to its high coercivity (5400 Oe) as compared with co-ferrite prepared via conventional powder sintering [106]. The facile and energy efficient thermolysis technique for synthesizing monodispers MFe$_2$O$_4$ (M = Mn, Fe, Co, Ni and Zn) nanoparticles provides excellent size distribution and better control over the size of nanoparticles from 2 to 16 nm. The magnetic properties of the nanoparticles have a strong correlation with the size and the divalent electronic configuration of M$^{2+}$ cations. The blocking temperature for nanoparticles increases with particle size and for CoFe$_2$O$_4$ nanoparticles a large increment in the blocking temperature is observed, because of the strong magnetic couplings originating from Co$^{2+}$ lattice sites [107]. Based on the one-ion crystalline-field model, the strong anisotropy of Co$^{2+}$ ions at the B-site originates from incompletely quenched angular momentum, which is attributed to the interaction of the electronic structure of Co$^{2+}$ ions with the crystal field [108]. CoFe$_2$O$_4$ (CFO) is an important spinel ferrite with Curie temperature 793 K, and shows a relatively large magnetic hysteresis. Now-a-days, nano-dimension spinel ferrites have drawn a considerable scientific and technological attention because of their applications in high-density magnetic recording media [106, 109], magnetic fluids [110], catalysts [111], gas-sensor [112-114], high-performance electromagnetic and spintronic devices [115-117]. The method of preparation, chemical composition, sintering temperature and time with sintering atmosphere strongly affect the physical properties of the CFO nano-ferrite. Among all the spinel ferrites known today, cobalt ferrite is of particular interest because of its high saturation magnetization, excellent chemical stability, mechanical hardness, and high cubic magneto-crystalline anisotropy [118-122]. From the detailed literature survey, it is clear that some work on the synthesis of nano-ferrites by high energy ball milling [123-124] high coercivity induced by mechanical milling of ferrite powder [125] and effect of milling time on structural and magnetic properties of nano-crystalline CFO has been reported [126].

**1.19.3 Manganese ferrite (MnFe$_2$O$_4$)**

The tailoring of physical properties of the spinel ferrites is generally governed by the choice of the cations and their distribution between tetrahedral and octahedral sites of the structure. The electrical and magnetic properties of spinel ferrites depend on the cations-distributions at different atomic sites of the structure [127-129]. The spinel structure of MFe$_2$O$_4$ (MFO) with space group Fd3m is generally characterized by its cubic unit cell containing eight
formula units. Each cubic unit cell (with close packing of thirty two oxygen anions) has twenty four cations located in eight of the sixty four tetrahedral sites (M) and sixteen of the thirty two are located at the octahedral sites (B-site) [130]. Manganese ferrite has 80% normal spinel structure (i.e., 20% of Mn$^{2+}$ ion occupy the octahedral site along with Fe$^{3+}$ ions). Neel temperature ($T_N$) of the material is reported to increase with the decrease in particle size and the prediction is consistent with the finite size scaling model [131-133]. The $T_N$ for bulk MFO has been reported to be 300 °C. With decrease in particle size to nano range the highest $T_N$ is reported to be 400°C for an average particle size of 50nm. With further decrease in particle size $T_N$ further decreases gradually to 320°C for an average particle size of 4nm. The variation in the Neel temperature with particle size is reported to be the consequence of cation distribution among the tetrahedral and octahedral sites of the spinel lattices [134]. Such type of effect has also been observed in the case of mechanically activated MnFe$_2$O$_4$. In the recent years, nano-ferrites have drawn a considerable scientific and technological attention because of their applications in high-density magnetic recording media, magnetic fluids [110], catalysts, gas-sensor[135], PEG-coated folic acid-modified superparamagnetic MnFe$_2$O$_4$ nanoparticles has been find their application in hyperthermia therapy and drug delivery [136], high-performance electromagnetic and spintronic devices and in magnetic hypothermia and drug delivery system [136]. MnFe$_2$O$_4$ particles yields via co-precipitation method shows a detestable site distribution Mn$_{0.33}$Fe$_{0.67}$O$_4$ and this phase can be irreversibly altered to Mn$_{0.60}$Fe$_{0.40}$O$_4$ by heating under inert gas at 670 K or to Mn$_{0.43}$Fe$_{0.57}$O$_4$ by heating in air at 470 K. Heat treatment in the air causes oxidation of some Mn$^{2+}$ to Mn$^{3+}$ and also a possible reason for Jahn-Teller distortion. $T_C$ decreases with particle size in a manner consistent with finite size scaling [137]. Among all the spinal ferrites known today, manganese ferrite is of particular interest because of its high saturation magnetization, excellent chemical stability, high mechanical hardness, and high cubic magneto-crystalline anisotropy [129].

1.19.4 Nano ceramic fabrication by ball milling

However, among the methods mentioned above, the mechanical alloying method has attracted much interest in recent years, due to its simplicity in the preparation of various interesting solid-state materials. MA takes advantage of the perturbation of surface-bonded species by pressure to enhance thermodynamic and kinetic reactions at room temperature or
at least at much lower temperatures than normally required to produce pure metals [138-141]. This is due to the energy transferred from the milling media to powder particles, continuously submitted to fracture and cold welding processes which will define their final morphology [140]. The particles synthesized usually have an equilibrated action distribution, a narrow size distribution economically viable and environmentally friendly. Some important components of the MA process are the raw materials, the mill, and the process variables [138]. Mechanochemical processing makes use of enhancement of chemical reactions of mechanical energy. Chemical reactions, which normally require high temperatures, can be thus activated during milling. The milling process causes a reduction of the particle size with a simultaneous disordered of the ion distributions [139].

As far as we know, no systematic study on the effect of milling time (size effect) on the structural and electrical properties of AFe$_2$O$_4$ (A=Ni, Co, Mn) nano-ceramics have been reported. In view of the importance of the material at nano-scale, we have carried out the synthesis of nano-ceramics of cobalt ferrite using planetary ball milling with different milling time, and studied the effect of milling time on structural and electrical properties of the AFe$_2$O$_4$ (A=Ni, Co, Mn) nano-ferrite.

1.19.5 Spinel ferrite –PVDF nanocomposites

All physical properties should be modified for better performances and wide application of PVDF. In case of a composite in a multi-phase system with PVDF, it can serve the purpose as individual component can’t compensate the required property. It is a well established fact that physical (permittivity, conductivity, resistivity, etc..), chemical and mechanical properties of PVDF can be modified by introducing some functional filler of metal/ceramics of different particle/ grain size. To achieve enhanced (high) dielectric properties (permittivity, piezo and pyro-electric, polarization), some attempts have been taken in preparing composite by introducing some ferroelectric or magnetic nano particle. PVDF/PZT nanocomposite film exhibits enhanced dielectric constant having no change in the dielectric loss in a frequency range of 100Hz-35MHz [142]. 50% BST 60/40/PVDF ceramic-polymer composite resulted in increased thermal strength of the composite [143]. BFO-PVDF nanocomposite films prepared by hot pressed method showed enhanced dielectric, conductive and magneto-capacitance as compared to pure BFO [144]. BFO and
Introduction

poly (vinylidene fluoride-trifluor-ethylene) [P(VDF+TrFE)] composite nanofibers fabricated by electro-spinning method revealed the coexistence of electric and magnetic hysteresis at room temperature [145]. PbTiO$_3$-PVDF composite revealed that the pyro-electric sensitivity increases with increases in PbTiO$_3$ content and the piezoelectric coefficient decreases slightly with a hydrostatic pressure [146]. PVDF/CCTO nanocrystal composite thick film resulted in high dielectric permittivity of 290 at 125°C at 100 Hz and dielectric constant increases with CCTO content, but there was a decrease in dielectric breakdown which limits its application at higher voltage [147]. Sr$_{0.7}$Ba$_{0.3}$Nb$_2$O$_6$ ceramic nano-powder-PVDF composite showed improved dielectric properties and the pyroelectric coefficient increases from 24μC/cm$^2$K in pure polymer to 40 μC/cm$^2$K in composite [148]. The low and high temperature dielectric properties of poly(vinylidene fluoride)/Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$ composite affected by the filler size and concentration [149]. The homogenously dispersed Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ particle of the dimension of 10-20nm in Poly(vinylidene-fluoride) matrix shows giant magneto-dielectric effect in 0-3 connectivity nanocomposite films. In this nanocomposite the polarization decreases with increase in filler concentration, whereas magnetization increases with increase in filler concentration [150]. Simple 0-3 type particulate polymer-based ME composite with magnetic nanoparticle [e.g. CFO, NiFe$_2$O$_4$, Fe$_3$O$_4$, and Terfenol-D] embedded in a polymer matrix (e.g. PVDF and Polyurethane) is of technological interest because of its easy processing. A (PVDF-TrFE) copolymer matrix composite with dispersed magnetic NFO nanoparticle presented a ME response of around 40mVcm$^{-1}$.Oe$^{-1}$ [151-152]. The enhanced dielectric parameter with magneto-dielectric property shows encouraging results in the lead free xPVDF-(1-x)(0.8BNT-0.2CFO) polymer nanocomposite for smart device application [153]. The presence of low content of nanoparticles in the composite of CoFe$_2$O$_4$/PVDF-TrFE significantly improves the polarization and piezoelectric responses of the copolymer matrix, demonstrating that low filler content nanocomposites are promising candidates for room temperature piezoelectric and ferroelectric applications. The magneto-electric response of the material is maximized for 72 wt% filler contents, with a $a_{33}$ value of 41.3 mV cm$^{-1}$ Oe$^{-1}$ for 72 wt% filler contents, with a $a_{33}$ value of 41.3 mV cm$^{-1}$ Oe$^{-1}$[152].
1.20 Objectives of the Proposed Work

The main objective of the present study (based on the large number of published works) has been given below.

a. Preparation of the AFe₂O₄ (A=Ni, Co, Mn) has been performed by a high-energy ball mill method with different milling time in order to gain time, energy and homogeneity. The ceramic-polymer nanocomposites fabricated by solvent casting

b. Structural and microstructural studies of the prepared compounds are carried to find out the phase formation, crystal structure and particle size of the different time milled compounds as well as the ceramic polymer nano-composite.

c. To understand the effect of milling time in different time milled sample and the effect of filler concentration in the ceramic-polymer composite, studies of dielectric properties (dielectric constant and tangent loss), over a wide range of frequency and temperature are carried out.

d. To analyze the electrical properties of the compounds as well as ceramic-polymer composite by complex impedance spectroscopy (CIS) to explore the structure-property relationship.

e. To study the relaxor, and related properties in a wide range of temperature to understand the possible mechanism behind the dielectric anomaly of the compounds as well as the ceramic polymer composite.

f. In order to investigate the relaxation behavior of dipoles and to obtain information about free charge carriers, the studies of complex impedance, complex electric modulus, relaxation and conductivity process of the materials are carried out.

g. To study the electrical polarization, magnetic properties as a function of magnetic field and the magneto-electric coupling coefficient of the fabricated sample.
1.21 Materials under Present Study

In the present study, the following nanocrystalline ferrites with different milling time along with ceramic polymer nanocomposite have been studied

(a) $\text{AFe}_2\text{O}_4 (\text{A=Ni, Co, Mn})$ with 30, 60 and 90h of milling
(b) $(1-x)\text{PVDF}-x(\text{AFe}_2\text{O}_4) (\text{A=Ni, Co, Mn and } x=0.05, 0.10 \text{ and } 0.15)$

1.22 Plan of the thesis

The brief description and the contents of the thesis (chapter wise) are given below

**Chapter-1** describes the brief introduction of different ferroic order and nano material with a special attention to spinel ferrite, its structure and importance. Summarized the reviews of work done on different synthesis technique to achieve the nanomaterial and also ferrite polymer multiferroic polymer nanocomposite. In the light of the literature survey, the main objective of the present work has been formulated.

**Chapter-2** deals with the sample preparation and describes the basic principles of different techniques of studies.

**Chapter-3** provides the structure, microstructure by X-ray diffraction technique, Scanning electron microscopy and high resolution transmission electron microscopy of the materials.

**Chapter-4** presents the detailed studies of dielectric properties of the materials.

**Chapter-5** provides an extensive study of electrical properties such as complex impedance spectroscopy and complex modulus spectroscopy of the entire compound as well as ceramic polymer nanocomposite.

**Chapter-6** provides the temperature and frequency dependent conductivity of the compound as well as ceramic polymer nanocomposite.

**Chapter-7** provides the magnetic properties of the compound as well as the multiferroic properties of the fabricated polymer nanocomposite.

**Chapter-8** provides the brief summary, conclusion and future scope of the work.