CHAPTER- I

General Introduction

1.1 Introduction to ferrite materials:

Among the magnetic oxide, the ferrite (ferromagnetic) materials are the important class of ferrite from point of view of their versatile application and academic point of view. They have been extensively studied for their structural, electrical and magnetic properties from last six to seven decades [1].

Ferrite consists of iron oxides (Fe₂O₃) and metal oxide (MO), virtue of their structure can accommodate variety of cations at available sites, bringing wide variation in their properties. Ferrite exhibits unique and interesting electrical and magnetic property which depend on various factors, such as elemental composition synthesis methods, synthesis condition, amount of dopant/substituent [2, 3]. Ferrites are ferromagnetic materials and are used in both soft and hard magnetic applications. Soft ferrites are characterized by the chemical formula MO.Fe₂O₃, with M being a transition metal element, e.g. iron, nickel, manganese or zinc. Hard ferrites are permanent magnetic materials, based on the crystallographic phases. Hard ferrites exhibit hexagonal crystal structure and a relatively high value of the anisotropy constant, yielding the necessary ingredients for a permanent magnet material. The easy axis of magnetization is along the hexagonal c-axis. Ferrites have many applications, which are in great demand, they can be used as magnetically guided drug delivery, magnetic resonance imaging etc. [4, 5]

The important electrical and magnetic properties of the ferrite materials, which decide the application areas, are generally governed by chemical compositions, preparative conditions and preparative parameters, method of preparation, type and
amount of substituent [6]. Thus, the chemical aspects of the ferrite have become most important in the design and preparation of ferrite materials. The ceramic method [7, 8] is commonly used for the synthesis of ferrites. This method is most economical and convenient.

1.2 Classification of Ferrite Materials:

According to magnetization ferrite materials are classified into two major groups (i) Soft ferrite (ii) Hard ferrite

1.2.1 Soft Ferrite

Soft ferrites are class of magnetic material which easily magnetize and demagnetize, they possess low coercive field. The low coercivity means the material's magnetization can easily reverse direction without dissipating much energy (hysteresis losses), while the material's with high resistivity prevents eddy currents in the core, another source of energy loss. Soft ferrites have certain advantages over other electromagnetic materials includes their inherent high electrical resistivity which result in low eddy current losses over wide frequency range. The most common soft ferrites are manganese-zinc (Mn-Zn) with the formula \( \text{Mn}_x\text{Zn}_{(1-x)}\text{Fe}_2\text{O}_4 \), Cobalt-Zinc (Co-Zn), Nickel-zinc (Ni-Zn) with the formula \( \text{Co}_x\text{Zn}_{(1-x)}\text{Fe}_2\text{O}_4 \) and \( \text{Ni}_x\text{Zn}_{(1-x)}\text{Fe}_2\text{O}_4 \) exhibit higher resistivity, higher permeability and saturation induction. Ferrites that are used in transformer or electromagnetic cores contain nickel, zinc, and manganese compounds. Some of the low frequency applications of soft ferrites include magnetic recording head, inductor and transformer core, filter cores magnetostrictive vibrator etc [9].

The characterization of soft and hard ferrites is based upon some following important parameters like
1) The residual magnetism (remanence/coercivity) $M_r$, when the external field is removed.

2) The saturation flux or maximum magnetic field that can be induced ($M_s$).

3) Coercive force ($H_c$), the value of the external field applied in the negative direction to demagnetize it.

### 1.2.2 Hard Ferrite

Magnetic hardness is due to fine particles having shape and crystalline anisotropy. A large crystalline anisotropy is characteristics of hard ferrites. Hence a large coercivity is almost an inherent property of hard ferrite. Barium and strontium ferrites are widely studied hard ferrites. The coercivity of these materials is more than 3000 Oe which is far in excess compared to other materials. The hard ferrites (Hexagonal ferrite) are used for constructing permanent magnet. These materials are ferrimagnetic and considering the proportion of iron within the material have quite a low remanence. On the basis of crystallographic aspects, the ferrites are classified into three major types. (1) Spinel (2) Garnet (3) Hexagonal. All of them are cubic in structure. Their parameters are given in Table below.

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Parameter</th>
<th>Hexagonal</th>
<th>Garnet</th>
<th>Spinel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Molecular Formula</td>
<td>$M(\text{Fe}<em>{12}\text{O}</em>{19})$</td>
<td>$M_3(\text{Fe}<em>5\text{O}</em>{12})$</td>
<td>$M(\text{Fe}_2\text{O}_4)$</td>
</tr>
<tr>
<td>2</td>
<td>Lattice Constant (Å)</td>
<td>5.8303</td>
<td>12.376</td>
<td>8.38</td>
</tr>
<tr>
<td>3</td>
<td>Curie Temp. (K)</td>
<td>673K</td>
<td>553K</td>
<td>690K</td>
</tr>
<tr>
<td>4</td>
<td>Electrical Resistivity</td>
<td>$1 \times 10^6$</td>
<td>$1 \times 10^{14}$</td>
<td>$1 \times 10^8$</td>
</tr>
<tr>
<td></td>
<td>(Ω-cm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Saturation Magnetization</td>
<td>60 emu/gm</td>
<td>36emu/gm</td>
<td>89emu/gm</td>
</tr>
</tbody>
</table>
The orbital and spin motion of electrons give rise to the origin of magnetism. The way in which electrons interacts with one another is also responsible for magnetism. On the basis of the interaction of electrons, the magnetic behavior of materials can be classified into the following six major groups.

(1) Diamagnetism (2) Paramagnetism (3) Ferromagnetism (4) Ferrimagnetisms
(5) Antiferromagnetism (6) Superparamagnetism [10].

1.2.3 Diamagnetism:

Diamagnetism is an inherent property of the orbital motion of the individual electron in a field. Since it is even a weaker effect it is only observed when the atom does not have a net spin or orbital moment. The orbital motion even though compensated sets up a field opposite to the applied field in a manner similar to the back e.m.f of Lenz's Law. The effect leads to a negative susceptibility or the actual lowering of the net moment in the material as an external field is applied. Diamagnetism is so weak an effect that a small paramagnetic impurity can offer mask out the effect.

1.2.4 Paramagnetism:

There are several known theories of paramagnetism, which are valid for specific types of materials. The Langevin model which is true for materials with non-interacting localized electrons, states that each atom has a magnetic moment which is randomly oriented as a result of thermal agitation. The application of a magnetic field creates a slight alignment of these moments and hence a low magnetization in the same direction as the applied field. As temperature increases, the thermal agitation also increases and it becomes harder to align the atomic magnetic moments and hence the susceptibility ($\chi$) also decreases. This behaviour is known as the Curie law and law is given by equation 1.1
\[ \chi = \frac{c}{T} \]  

Where C- material constant called the Curie constant, T –Absolute temperature (K)

In this types of ferrite Curie law is a special case of the more general Curie- Weiss law, which incorporates a temperature constant (\(\theta\)) and derives from Weiss theory, proposed for ferromagnetic material, that incorporates the interaction between magnetic moments.

\[ \chi = \frac{c}{T-\theta} \]  

(1.2)

In this equation, \(\theta\) can either be positive, negative or zero.

**1.2.5 Ferromagnetism:**

Ferromagnetism is only possible when the atoms are arranged in lattice and atomic magnetic moments can interact to align parallel to each other. Weiss postulated the presence of magnetic domains within the material, which are regions where the atomic magnetic moments aligned. The movement of these domains determines how the material responds to a magnetic field and as consequence the susceptibility is a function of applied magnetic field. Only Fe, Co, and Ni are ferromagnetic at and above room temperature. As ferromagnetic materials are heated, then thermal agitation of the atoms means that degree of alignment of the atomic magnetic moments decreases and the saturation magnetization also decreases. Eventually, the thermal agitation becomes so great that the material becomes paramagnetic; the temperature of this transition is the Curie temperature (\(T_C\)).

**Weiss Theory of Ferromagnetism:-** In 1907 French Scientist Weiss presented spontaneous magnetization postulating that elementary dipole moment interact each other as shown in Fig1.1(a) This interaction is called molecular field \(H_m\). It acted in addition external applied field H. This molecular field is due to magnetization of
surrounding molecule. Weiss assumed that molecular field $H_m$ to be function of magnetization $M$ as $H_m = \gamma M$ where $\gamma$ = molecular field constant. There total internal field $H_i = H + H_m = H + \gamma M$. In Ferromagnetism spontaneous magnetization take place only below ferromagnetic Curie temperature $T_c$. Above $T_c$ material behave like paramagnetic material. They have well defined susceptibility $\chi_m$ that follows Curie - Weiss law as $\chi_m = \frac{C}{T - \theta}$ where, $C$ = Curie constant, $\theta$ = Paramagnetic Curie temperature. Fig 1.1(b) shows hysteresis loop for ferromagnetic material taken through cycle of magnetization that means subjected to forward and reverse saturation magnetization (hysteresis loop).

![Hysteresis Loop](image)

**Fig 1.1** Magnetic flux density versus the magnetic field strength for ferromagnetic

From saturation point $S$ in Fig.1.1 as the $H$ field is reduced, by reversal of field direction, the curve does not retrace its original path. A hysteresis effect is produced in which the $B$ field lags behind the applied $H$ field or decreases at lower rate. At zero $H$ field (point $R$ on the curve), there exists a residual $B$ field that is called the remanence flux density ($B_r$), the material remains magnetized in the absence of an external $H$ field [11].
1.2.6 Ferrimagnetisms:

Snoek (1936, 1947) in Holland obtained very interesting properties in a new class of oxide materials called ferrites that were very useful at high frequencies. Now, a dilemma had arisen in accounting for the magnetic moment of a ferrite such as magnetite, Fe$_3$O$_4$ or FeO.Fe$_2$O$_3$. The theoretical number of unpaired electrons for that formula was 14, that is, 5 each for each of the Fe$^{+++}$ ions and 4 for the Fe$^{++}$ ion. Neel then extended his theory to include ferrites. There were still two different lattice sites and the same negative exchange interaction. The difference was that in the case of antiferromagnetics, the moments on the two sites were equal while in the case of the ferrites they were not and so complete cancellation did not occur and a net moment was the difference in the moments on the two sites [12].

1.2.7 Antiferrimagnetism:

In ferromagnetism, the interaction of atomic spin moments was a positive one meaning that the exchange interaction aligned neighboring spins parallel in a magnetic domain. Neel (1932) in his study of the paramagnetic susceptibility of certain alloys, noticed that they did not follow the Curie law at low temperatures but did obey the Curie-Weiss law at high temperatures

\[ \chi = \frac{C}{T+\Theta} \]  

Where \( \Theta \) = experimentally determined constant. Also

\[ \chi = \frac{C}{T-T_N} \]  

Where \( T_N \)= Neel Temperature.

Where the extrapolation of the high temperature linear slope of \( 1/\chi \) vs \( T \) resulted in a negative value or a negative at Curie point

1.2.8 Superparamagnetism:
This is a unique class of magnetic materials. They are single domain particles that behave like ordinary ferromagnetic materials below Curie temperature, $T_C$, as they have very large magnetic susceptibilities, are saturated in moderate magnetic fields and display coercivity and remanence. Above $T_C$, however superparamagnetic materials behave like ordinary paramagnetic material as they display no hysteresis. [13]

**Fig 1.2  Relationship between various magnetic quantities**

**1.2.9 Magnetostrictive property of ferromagnetic materials:**

Magnetostriction is a property of ferromagnetic materials to undergo change of their physical dimensions when subjected to a magnetic field. This effect was first identified in 1842 by James Joule when observing a sample of nickel. This is the property which allows magnetostrictive materials to convert magnetic energy into kinetic energy. This property is used for the building of both actuation and sensing devices. It is often quantified by the magnetostrictive coefficient '$\lambda$' which is the fractional change in length as the magnetization of the material increases from zero.
to the saturation value. The coefficient ‘λ’ may be positive or negative, and is usually on the order of $10^{-5}$ [14].

1.2.10 Magnetostriction:

The mechanism of magnetostriction, on a macroscopic level may be segregated into two distinct processes. The first process is dominated by the fields, second, is by rotation of the domains. These two mechanisms allow the material to change the domain orientation which in turn causes a dimensional change. Since the deformation is isochoric there is an opposite dimensional change in the orthogonal direction. The basic idea is that, the rotation and movement of magnetic domains causes a physical length change in the material and the elongation of a material, due to rotation and reorientation of dipoles as shown in Figure 2.3. On the microscopic level it may be said that magnetostriction is due to the phenomenon of spin-orbit coupling. This phenomenon, observed in materials subjected to magnetic fields may be erroneously perceived as magnetostriction. This is the form of effect that is seen due to the demagnetizing factor ($N_d$) of the sample, in the direction of saturation magnetization. This factor depends on the geometry of the sample and is lesser if the sample is longer in the direction of magnetization. The greater the value of $N_d$, the greater is the magnetostatic energy, and hence the tendency to elongate in the direction of the field and reduce the magneto static energy [15].

$$\text{Energy Density}= \frac{N_d M_s^2}{2}$$

1.6

Where, $M_s$ is saturation magnetization. This property is important composite materials to show better magnetoelectric effect. The material having more magnetostrictive coefficient, shows large magnetoelectric (ME) effect.
1.3 Application of ferrite:

Some of the applications of ferrites are given below

1. Magnetic Sensors: These are used for temperature control and these can be made using ferrite with sharp and definite Curie temperature. Position and rotational angle sensors (proximity switches) have also been designed using ferrites.

2. Magnetic Shielding: A radar absorbing paint containing ferrite has been developed to render an aircraft or submarine invisible to radar.

3. Ferrite Electrode: Because of their high corrosion resistance, ferrites having the appropriate conductivities have been used as electrodes in applications such as chromium plating.

4. Pollution Control: Ferrites are used to scavenge pollutant materials such as mercury from waste streams.

5. Entertainment Ferrites: Ferrites are widely used in radio and television circuits. Typical applications include antenna, deflection yoke, fly-back transformers, and SMPS transformers for power applications [16]

1.2 Introduction to Ferroelectric Materials:

The ferroelectricity and piezoelectricity in ceramic materials began in the early 1940s. Rochelle salt (sodium potassium tartrate tetrahydrate) was first prepared by Elie Seignette in La Rochelle, France, for medicinal purposes. The
phenomenon of ferroelectricity was discovered in 1921 by J. Valasek who was investigating the dielectric properties of Rochelle salt (NaKC\_4H\_4O\_6.4H\_2O). It become customary to call “ferroelectricity” the phenomenon exhibited by the crystal and “ferroelectric” crystal themselves. The reason is due to a formal similarity of the ferroelectric phenomenon with that of ferromagnetism. Ferromagnetic material shows spontaneous magnetization and hysteresis effect in relationship between magnetization and magnetic field, ferroelectric shows spontaneous electric polarization and hysteresis effect in relationship between dielectric polarization and electric field [17]. Fig 1.3 Shows variation different piezoelectric parameter when material is taken through cycle of polarization. The knowledge of the ferroelectric nature of ceramic BaTiO\_3 proved to be invaluable when it was discovered by Gray in 1945 that an external electric field could orient the domains within the grains, thus producing polarization.

![Graph showing piezoelectric parameter variation](image)

**Fig 1.4 The variation of piezoelectric parameter with cycle of electric field.**

Ferroelectric ceramic is a material that acts as very similar to a single crystal possessing both ferroelectric and piezoelectric properties [18]. Science the discovery of ferroelectricity in single-crystal materials (Rochelle salt) in 1921 and its subsequent extension into the realm of polycrystalline ceramics barium titanate (BaTiO\_3) during the early to mid-1940’s there has been a continuous succession of
new materials and technology developments that have led to a significant number of industrial and commercial applications[19].

1.2.1 Types of ferroelectrics:

For number of years, the phenomenon of ferroelectricity was known to occur in a rather limited number of crystals. At this stage various classifications of the ferroelectric crystal is proposed. Thus two main types are: Naturally existing and Artificial.

Naturally existing: 1 Rochelle salt (NaKC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}.4H\textsubscript{2}O) 2 Quartz

Artificial Ferroelectric Materials: According to chemical point of view they are classified as (1) phosphate (2) arsenate (3) double oxide (4) Sulphate (6) borate (7) nitrate (8) titanate.

Ex:- Lithium ammonium tartrate, Potassium di-hydrogen phosphate or arsenate, Barium titanate, Potassium niobate[17]

1.2.3 General feature of ferroelectricity:

- **Piezoelectricity:**

Piezoelectricity, a property possessed by a select group of materials, was discovered in 1880 by Jacques and Pierre Curie [20]. The name “piezo” is derived from the Greek, meaning “to press”. Hence, piezoelectricity is the generation of electricity as a result of a mechanical pressure. Cady defines piezoelectricity as “electric polarization produced by mechanical strain in crystals belonging to certain classes, the polarization being proportional to the strain and changing sign with it [21]. An understanding of the concept of piezoelectricity in solids begins with an understanding of the internal structure of the material; for purposes here, consider a single crystallite. This crystallite has a definite chemical composition and, hence, is made up of ions (atoms with positive or negative charge) that are constrained to
occupy positions in a specific repeating relationship to each other, thus building up the structure or lattice of the crystal. The smallest repeating unit of the lattice is called the unit cell. The specific symmetry possessed by the unit cell determines whether it is possible that piezoelectricity to be exist in the crystal or not. The elements of symmetry that are utilized by crystallographers to define symmetry about a point in space, e.g., the central point of a unit cell, are (1) center of symmetry, (2) axes of rotation, (3) mirror planes (4) Combinations of these. A lack of a center of symmetry is all-important for the presence of piezoelectricity. As there is lacks of center of symmetry, where by a net movement of the positive and negative ions with respect to each other (as a result of the stress) produces electric dipoles, i.e., polarization. For piezoelectricity, the effect is linear and reversible, and the magnitude of the polarization is dependent on the magnitude of the stress and the sign of the charge produced is dependent on the type of stress [22].

- **Piezoelectric Effect:**

In piezoelectric crystals, the positive and negative electrical charges are separated but symmetrically distributed. The crystal overall is electrically neutral. When a stress is applied, this symmetry is disturbed, and the charge asymmetry generates a voltage. On a microscopic scale, piezoelectricity results from a non uniform charge distribution within a crystal’s unit cells. When such a crystal is mechanically deformed, the positive and negative charge centers displace by differing amounts. So while the overall crystal remains electrically neutral, the difference in charge center displacements results in an electric polarization within the crystal. Electric polarization due to mechanical input is perceived as piezoelectricity. Piezoelectricity – application of pressure produces current.
Application of electric field produces polarization in piezoelectric material. We define polarizabilities $\alpha$ of atoms of materials as ratio between dipole moment (permanent or induced) of the atom and the electric field acting upon it: $\alpha=\mu/F$.

The field $F$ is generally given by Lorentz’s formula for internal field acting on a dipole located in a lattice of dipole with cubic symmetry: $F= E + \frac{4\pi}{3} P$. This formula leads to Claussius-Mosotti equation for the dielectric constant ($\varepsilon$):

$$\frac{\varepsilon - 1}{\varepsilon - 2} = \frac{4\pi}{3} N\alpha$$

Where, $N$ is number of dipole per unit volume. From above equation we have $\varepsilon = \frac{1+(8\pi/3)N\alpha}{1-(4\pi/3)N\alpha}$. From this, it follows that the dielectric constant $\varepsilon$ become infinite, corresponding to finite polarization for zero applied field, when $N\alpha = \frac{3}{4\pi}$. For example, putting this value $1-\frac{4\pi}{3}N\alpha = \frac{3}{C}(T-T_0)$.

This is Curie-Weiss Law for dielectric constant $\varepsilon \equiv \frac{C}{T-T_0}$ [15].

- **Electrostriction:**

Electrostriction is another electromechanical effect that exists in ferroelectric ceramics. In electrostriction, the sign of the deformation that occurs with an electric field is independent of the polarity of the field and is proportional to even powers of the field. In piezoelectricity, the deformation is linear with respect to the applied field and changes sign when the field is reversed as shown in fig1.5. This means in practical terms that electrostriction produces an expansion in most materials in the direction of the field regardless of its polarity, and this expansion relaxes back to zero when the field is removed [23].
At rest compression induces voltage applied voltage induces expansion

- **Spontaneous polarization in ferroelectric materials:**

Ferroelectric materials are characterized by a reversible spontaneous polarization in the absence of an electric field [24]. Spontaneous polarization in ferroelectric arises from noncentrosymmetric arrangement of ions in its unit cell that produces an electric dipole moment. Adjacent unit cells tend to polarize in the same direction and form a region called a ferroelectric domain. The most common ferroelectrics have the ABO$_3$ perovskite structure. Most ferroelectric materials undergo a structural phase transition from a high-temperature no ferroelectric (or paraelectric) phase into a low-temperature ferroelectric phase. The symmetry of the ferroelectric phase is always lower than the symmetry of the paraelectric phase. The temperature of the phase transition is called the Curie point, $T_C$. Above the Curie point the dielectric permittivity ($\varepsilon$) falls off with temperature according to Curie–Weiss law

$$\varepsilon = \varepsilon_0 + \frac{C}{T - T_0}$$  \hspace{1cm} (1.5)

Where $C$ is the Curie constant, $T_0$ ($T_0 < T_C$) is the Curie–Weiss temperature, $\varepsilon_0$ – dielectric permittivity at absolute zero temperature. Above the Curie temperature, these materials have a centrosymmetric structure and therefore lose all spontaneous polarization. In this state, the material is termed paraelectric [25]. A Piezoelectric material converts mechanical (strain) energy to electrical energy and vice-versa. Thus piezoelectric material transduces mechanical energy into electrical energy and
hence called “transducer” [26]. In piezoelectric crystal charges may be formed on surface as result of temperature change when no mechanical stress is present. These crystal are pyroelectric crystal.

1.2.4 Applications ferroelectric materials:

Applications of ferroelectric materials have expanded into many fields since the discovery of the effect by the Curie brothers in 1880-1881. Applications can be grouped into three categories depending on physical changes.

1. Mechanical to Electrical

- Force, Pressure, and acceleration sensors:
- pressure gauges, car impact & skid (yaw rate) sensors
- High Voltage - Low Current Generators, i.e., Piezo-spark ignition:
- stoves, grills, small engines, cell phone bombs
- Platform Stabilization Sensors
- Echo Imaging
- SONAR (Sound Navigation And Ranging)
- Echo Sounding
- Medical Imaging (Sonography, Echocardiography

2. Electrical to Mechanical

- Ultrasonic motors
- Small Vibration Shakers
- Microactuators and High Precision Macro Actuators
- Inkjet Print Heads
- Audio Transducers (microphones & speakers)
- Piezoelectric Refrigerators (NASA)
- Drilling and Machining
3. Cavitations-related (liquids)

- Sonochemistry & Sonoluminescence
- Sonocrystallization (big pharma)
- Ultrasonic Cleaning
- Atomization, Vaporization
- Spray Drying

Piezoelectric devices grouped into four general categories, depending of what type of physical effect is used: generators, sensors, actuators, and transducers. Generators and sensors make use of the direct piezoelectric effect, meaning that mechanical energy is transformed into a dielectric displacement [27].

1.3 Introduction to composites materials:

Modern science and technology applications demand for new properties that rarely can be accomplished in single phase structures. Therefore, various combinations of dissimilar materials in composites are designed, produced, and investigated, while the simulation techniques able to predict their functional properties have been continuously developed. The composite electroceramics have a remarkably wide variety of practical applications [28].

Recent thrust on developing multifunctional for high performance solid state device applications are a driving force to work on multiferroic materials. Multiferroic materials that combine spontaneous magnetization with ferroelectric polarization are of tremendous technological and fundamental interest. Multiferroic are those materials, which possess more than primary ferromagnetic properties (i.e., charge, spin and strain) in a single-phase material so that it can enable to tune magnetization by the application of electric field and vice versa. This effect is called magnetoelectric effect. Due to the coexistence of more than ferromagnetic properties
such as (spontaneous magnetization, polarization, strain etc.), these materials have received a considerable attention for various multifunctional devices such as multiple-state memory elements, electric field controlled ferromagnetic resonance devices, transducers, spintronics etc[29]. Though various research activities have been initiated by different research groups around the globe to overcome the above problems, not much success has been achieved on enhancing the electromagnetic coupling coefficient. The magnetoelectric coupling coefficient occurs either directly between the two order parameters or indirectly via strain. Moreover, it has been found that ferroelectric and ferromagnetic in single-phase materials with large and robust spontaneous magnetization and polarization is rare; they tend to exhibit rather weak ferromagnetism or is not strong enough insulators to sustain ferroelectric polarization at room temperature. In fact, the coexistence of ferroelectricity and ferromagnetism is difficult to achieve in single phase materials. Alternatively, multiferroic composites are likely to possess a large magnetoelectric coupling factor with high value of magnetization and Polarization, which is desirable for device applications as compared to the single-phase counterpart. The strong magnetoelectric coupling factor is due to effective strain-mediated magnetoelectric coupling giving rise to the giant product property of the piezoelectric and magnetostrictive effect of both the components. To obtain maximum electromagnetic coupling coefficient, various composite systems have been fabricated and characterized in different forms such as (1) Multilayer thin film of ferroelectric and magnetic oxides, (2) Bulk composite: where second phase particles (ferroelectric particles)embedded in a primary matrix phase(ferrite phase) (3) Three phase ME composites, where ferroelectric and ferromagnetic oxides dispersed in polymer matrix [30]. In view of the above several attempts have been made by
researchers to develop different types of new ME composites [31] ME materials consist of ferromagnetic material and piezoelectric material.

1.3.1 Application of Composites:

The ME effect is a tool for the conversion of energy from magnetic to electric form or vice versa. Tellegen proposed a gyrator using a ME material before the discovery of any ME materials. The ME material can be used in binary data storage devices. Such a memory will be an effective ‘read only’ memory, since the reading can be done at very high frequencies. The ME composites can be used as ME transducers in recording heads and electromagnetic pick-ups. Apart from these applications, some of the applications of composites are listed below.

(1) microwave antennas (2) sensors (3) resonators (4) oscillators (5) filters (6) phase shifters (7) attenuators (8) amplifiers (9) microwave resonance devices (10) micro/nano electromechanical systems (11) signal processing (12) Passive Magnetic sensor (13) Active D.C Magnetic sensor (14) Geomagnetic sensor [32].

1.4 Literature Survey:

Historically BaTiO$_3$–CoFe$_2$O$_4$ composites were first obtained in 1972 by Van Suchtelen. Types of materials that undergo ME multiferroic are Single material or composite. Theoretically the magneto electric effect came into picture in 1894 when Curie discussed correlation of magnetic and electric properties in low symmetry crystals.

1.4.1 Cobalt ferrite:

Among the different spinel type ferrite material, cobalt ferrites are of great importance because of their excellent chemical stability, good mechanical hardness, high electrical resistivity, low eddy current and dielectric losses, high coercivity, moderate saturation magnetization, positive anisotropy constant and high
magnetostriction [33]. Owing to their important properties cobalt ferrite are widely used magnetic materials in high frequency applications.

Many investigators have focused their attention on cobalt ferrite because Cobalt ferrite has interesting magnetic and electrical properties [34]. Cobalt ferrite is an inverse spinel ferrite, whose degree of inversion depends on method of preparation. Although, cobalt ferrite has been studied by several workers, manganese and Zinc substituted cobalt ferrite has not been studied for ME composites. Cobalt ferrite (CoFe$_2$O$_4$) is cubic ferrimagnetic oxides which have attracted attention because of their large permeability and high electrical resistivity. Cobalt is an important material because of its good magnetostrictive, magnetic and electrical properties which depend on the textural and morphological properties [35].

1.4.2 Barium titanate:

Barium titanate is the first ferroelectric ceramics and a good candidate for a variety of applications due to its excellent dielectric, ferroelectric and piezoelectric properties. Barium titanate is a member of a large family of compounds with the general formula ABO$_3$ called perovskites. Barium titanate was widely used in composites, electronic devices. [17-24]. Barium titanate has sharp phase transition from the paraelectric to ferroelectric state as temperature is increased (Fig 2.4). In BaTiO$_3$, the ferroelectric transition occurs at 120° C, which roughly corresponds to the peak in permittivity. Below the Curie temperature, the cubic structure changes to lower symmetry and there is a sharp decrease in dielectric constant. Above the Curie temperature $T_C$, the relative permittivity follows the Curie-Weiss law:
\[ \varepsilon_r = \frac{C}{T - T_c} \] where \( C \) is the Curie constant which has \( \text{value} = 1.54 \times 10^5 \, \text{degree} \). [12]

Much experimental work has been conducted to analyze the properties of the perovskite type ferroelectric materials in order to push forward the applicable progress. In recent years magneto-electric multiferroics have attracted tremendous interests due to their magneto-electric properties, originating from the coupling between ferroelectric and ferromagnetic order parameter. The combination of ferrite and ferroelectric shows magneto-electric property.

![Fig 1.6 Dielectric constant of BaTiO$_3$ as function of temperature](image)

**Fig 1.6 Dielectric constant of BaTiO$_3$ as function of temperature**

Strong magneto-electric effect (ME) was theoretically discussed by L.D. Landau in 1957. First experimental observation of the ME effect was reported in 1960 by Astrov, who found that electric field induces magneto-electric effect in Cr$_2$O$_3$. [28]

**Rupesh Devan et.al.** [36] Prepared (Ni–Co–Cu) ferrite/BTO composites. These electro-ceramic composites of ferrite and ferroelectric phases have the ability to show product and sum properties. The ME composites \((x)\) BaTiO$_3 + (1-x)$ Ni$_{0.93}$Co$_{0.02}$Cu$_{0.05}$Fe$_2$O$_4$ were prepared by double sintering ceramic technique. The
BTO was sintered at 900 °C and Ni$_{0.93}$Co$_{0.02}$Cu$_{0.05}$Fe$_2$O$_4$ was sintered at 800 °C for 10h. Samples were finally sintered at 1150 °C for 12 h. The dielectric constant increases with temperature, up to Curie temperature ($T_c$) and then decreases, which is normal behaviour, expected in most of the ferrites and ME composites. The dielectric constant was found to reduce with increase in ferrite content. The ac conductivity measurements indicate polaron hopping type conduction. The maximum static ME voltage coefficient ($dE/dH$)$_H$ of 431 $\mu$V cm$^{-1}$ Oe$^{-1}$

Shaikh et al. [37] investigated the electrical resistivity and Curie temperature of Zn substituted (Li$_x$Mg$_{0.4}$Zn$_{0.6-2x}$) Fe$_{2+x}$O$_4$ ferrites and found decrease in the resistivity with Zn content and then increase with further addition of Zn content. The Curie temperature was also found to be decreased linearly with the addition of Zn. For higher level substitution of Zn, the ‘A’ site magnetic ion became so diluted that the coupling between two lattices was diminished and the saturation magnetization gets dropped. An additional consequence of the weakening magnetic interactions was that the spin coupling could more easily be moved out of alignment by thermal energy vibrations so that, the Curie temperature decreased with Zn substitution.

Kamble et.al [38] prepared Co-Mn ferrite (CMFO) and Ba-Zr titanate (BZT) ferroelectric multiferroic composite with a view to increase the ME conversion factor. The presence of Mn$^{4+}$ ions in cobalt ferrite enhances the piezomagnetic property, which leads to increase in ME conversion factor of the composite. The addition of zirconium in barium titanate increases the piezoelectric property. The best ME coefficient was observed for 25 % Co-Mn ferrite and 75 % BZT ferroelectric composites. Extensive work was carried out on composites with
different types of ferrites and barium titanate in order to obtain large value of magnetoelectric effect [28-36].

**1.5 Objectives of present work:**

For preparation of ME composites, the choice of ferroelectric and ferrite phases depends on their Curie temperatures, good piezoelectric properties of piezoelectric phase and sufficiently high-piezomagnetic property of the magnetostrictive phase, high electromechanical and magneto mechanical coupling coefficients and structural comparability. For this a highly piezomagnetic insulator should be chosen as the magnetostrictive component in these particulate composites. The resistivity of the magnetostrictive phase should also be as high. Keeping this viewpoint in mind as no work has been reported in the literature for the structural, electrical and magnetoelectric measurement of \((\text{CoMn}_{0.2}\text{Zn}_{0.2}\text{Fe}_{1.6}\text{O}_4) + (1-x)\) BaTiO\(_3\) composite. Hence the intuition of the present work is to

1. To synthesize magnetoelectric composites of ferrite phase \(\text{CoMn}_{0.2}\text{Zn}_{0.2}\text{Fe}_{1.6}\text{O}_4\) and ferroelectric phase \(\text{BaTiO}_3\)
2. Study the structural properties of ferrite, ferroelectric and their composites.
3. Study the electrical and dielectric properties of ferrite, ferroelectric and composites.
4. Study the magnetic properties of ferrite, ferroelectric and their composites in order to enhance magnetoelectric behaviour of the composites.
5. Study the Magnetoelectric effect in composites.
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