Chapter - 1

Introduction of Magnetic Materials
1.1 Introduction of Magnetic materials

Material Science and engineering plays an imperative role in this modern age of science and technology. The drastic progress in the development and growth of electronic ceramics since the era of post Second World War II has played a major role in the transformation of the society from Steel Age to the Information Age. Nearly instantaneous satellite communications from coast to coast and around the world would not be possible without simultaneous advances in semiconductors, dielectrics, ferroelectrics, ferrites and optoelectronics. The continued developments in these fields have been matched, and perhaps eventually superseded with advances in superconducting ceramics, photonics, and optical waveguides and potentially in optical computing and information processing [1].

In connection with advances in communication technologies, magnetic ceramics have been investigated due to their vastly intriguing properties such as magnetization behaviour, high magnetic permeability and high electrical resistivity [2]. These intrinsic material properties have made them indispensably the most versatile engineering ceramics for high frequency applications including power transformers, antennas, faraday rotators, etc [3].

A magnetization ($M$) can occur as a result of more or less alignment of elementary magnets known as magnetic dipole (electron orbits or electron spins) present in a matter. In order to produce this alignment of magnetic dipole, an external magnetic field ($H$) is to be applied. When magnetization is relatively small, it increases proportionally with an applied field according to the relation, $M = \chi H$, where $\chi$ is the susceptibility per cm$^3$ [4]. Magnetism in the material can be classified in terms of the arrangements of magnetic dipoles in the solid and depending upon the sign and the value of susceptibility ($\chi$). These dipoles can be thought of, a little imprecisely, as microscopic bar magnets attached to the various atoms present.

1.1.1 Types of magnetic materials

Magnetic materials are divided into five groups namely; Diamagnetic, Paramagnetic, Ferromagnetic, Antiferromagnetic and Ferrimagnetic.
(a) **Diamagnetic Materials**

Materials with no elementary magnetic dipoles are known as diamagnetic. The magnetic susceptibility ($\chi$) of a diamagnetic substance is negative and very slightly less than 1 and of the order of $10^{-5}$. There is no appreciable variation of diamagnetism with temperature. In the absence of an applied magnetic field, each atom has net zero magnetic dipole moment. In the presence of an applied magnetic field, the angular velocities of the electronic orbits are changed. These induced magnetic dipole moments align themselves opposite to the applied field. Diamagnetism can be a big effect in superconductors and in artificial materials. Diamagnetic materials are repelled from either pole of a magnet. Water, Gold, Bismuth, Copper, Zinc, Mercury are examples of diamagnetic materials.

(b) **Paramagnetic Materials**

Paramagnetic solids are those in which some of the atoms, ions or molecules making up the solid possess a permanent magnetic dipole moment. These dipoles are isolated from one another. In the absence of an applied magnetic field, each atom has net non-zero (but weak) magnetic dipole moment. These magnetic dipole moments are randomly oriented so that the net macroscopic magnetization is zero. In the presence of an applied magnetic field, the magnetic dipoles align themselves with the applied field so that magnetic susceptibility, $\chi_m > 0$ and of the order less than $10^{-2}$. Paramagnetic materials are (weakly) attracted to either pole of a magnet. Examples of paramagnetic substances are Aluminium, Platinum, Lithium, Oxygen and in general all magnetically diluted solution of elements which have an incomplete atomic orbital.

(c) **Ferromagnetic Materials**

Ferromagnetic materials include iron, nickel and cobalt and compounds containing these elements. In the absence of an applied external magnetic field, each atom has very strong magnetic dipole moments due to uncompensated electron spins. Regions of many atoms with aligned dipole moments called ‘domains’. In the absence of an applied magnetic field, the domains are randomly oriented so that the net macroscopic magnetization is zero. In the presence of an applied magnetic field, the
domains align themselves with the applied field. The effect is a very strong one with $\chi_m \gg 0$.

Ferromagnetic materials are strongly attracted to either pole of a magnet. The permeability is very non-linear and it depends on the previous history of the material and it is much larger than the permeability of free space. The relationship, $B = \mu H$ can be illustrated by means of a magnetization curve (also called hysteresis loop). Where, $B$ is the magnetic flux density, $\mu$ is permeability and $H$ is magnetic field strength.

(d) **Antiferromagnetic Materials**

In antiferromagnetic materials, the magnetic moments of individual atoms are strong, but adjacent atoms align in opposite directions. The macroscopic magnetization of the material is negligible even in the presence of an applied field. Antiferromagnetic materials include Chromium and Manganese.

(e) **Ferrimagnetic Materials**

In the Ferrimagnetic materials, the magnetic moments of adjacent atoms are aligned opposite to each other, but there is incomplete cancellation of the moments because they are not equal. Thus, there is a net magnetic moment within a domain. In the absence of applied magnetic field, the domains are randomly oriented so that the net macroscopic magnetization is zero. In the presence of an applied magnetic field, the domains align themselves with the applied field. The magnetic effects are weaker than in ferromagnetic materials, but are still substantial. Such materials include oxides of Iron, Nickel, Cobalt and ferrites.

1.1.2 Ferrites

Ferrites or ferrimagnetic oxides (also known as ceramics containing compounds of iron) are dark brown or gray in appearance and very hard and brittle in physical character. They are prepared by heat-treating the various transition metal oxides or alkaline earth oxides with the ferric oxides [5]. The magnetic behaviour exhibited by the ferrites is quite different from ferromagnetism that is exhibited by metallic materials. Ferrites are non-conducting magnetic media so eddy current and
ohmic losses are less than for ferromagnetic materials. Ferrites are often used as transformer cores at radio frequencies (RF). Ferrites are most common in nature. From the daily iron oxide Fe₃O₄ (magnetite) formed at the surface of many iron-containing objects like fences, cars, doors, barbecue grills.

Ferrite exhibits ferrimagnetism due to the super-exchange interaction between electrons of metal and oxygen ions. The opposite spins in ferrite results in the lowering of magnetization compared to ferromagnetic metals where the spins are parallel. Due to the intrinsic atomic level interaction between oxygen and metal ions, ferrite has higher resistivity compared to ferromagnetic metals. This enables the ferrite to find applications at higher frequencies and makes it technologically very valuable. Their magnetic properties can greatly vary from one element to another, since the microscopic (atomic) structure is composed of two or more magnetic sublattices.

1.2 Classification of ferrites

Ferrites are classified according to magnetic properties and their crystal structure.

1.2.1 According to magnetic properties

Ferrites are often classified as "soft" and "hard" which refers to their low or high coercivity of their magnetism, respectively.

(i) Soft ferrites

Soft ferrites are ferrimagnetic materials with cubic crystal structure and they are characterized by chemical formula MO·Fe₂O₃, where M is a transition metal ions like Iron, Nickel, Manganese or Zinc. Manganese-Zinc ferrites are used in soft magnetic applications up to high frequencies of 10 MHz. Soft magnetic material is one that can be both easily magnetized and demagnetized, so that it can store or transfer magnetic energy in alternating or other changing wave forms (sine, pulse, square, etc). At high frequency metallic soft magnetic materials simply cannot be used due to the eddy current losses. Therefore, soft ferrites, which are ceramic insulators, become the most desirable material for example in telephone signal transmitters and
receivers and in switch mode power supplies (referred as DC-DC converters). For such type of application the driving force to increase frequency is to allow miniaturisation.

(ii) Hard ferrites

Permanent ferrite magnets are made up of hard ferrites, which have a high coercivity and high remanance after magnetization. These ferrites are composed of iron and barium or strontium oxides. In a magnetically saturated state they conduct magnetic flux well and have a high magnetic permeability. This enables these ceramic magnets to store stronger magnetic fields than iron itself. They are cheap, and are widely used in household products such as refrigerator magnets. The hexagonal ferrite structure is found in both BaO·6Fe₂O₃ and SrO·6Fe₂O₃, but Sr-M hexaferrite has slightly superior magnetic properties.

1.2.2 According to crystal structure

The ferrites consist dominant compound of Fe₂O₃, are divided into four groups namely Spinal, Garnet, Ortho and hexagonal or magnetoplumbite ferrites. These ferrites are distinguished with respect to the molar ratio of Fe₂O₃ to other oxide components present in the ceramic as shown in Table 1.1.

Table 1. Classification of ferrites

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Types</th>
<th>Molar ratio</th>
<th>Representations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Spinel</td>
<td>Fe₂O₃ – 1MeO</td>
<td>MeO is a transition metal oxide</td>
</tr>
<tr>
<td>2</td>
<td>Garnet</td>
<td>5 Fe₂O₃ – 3 Me₂O₃</td>
<td>Me₂O₃ is a rare earth metal oxide</td>
</tr>
<tr>
<td>3</td>
<td>Ortho</td>
<td>AFeO₃</td>
<td>A is rare earth elements like Ho, Dy, Er, Y, Yb</td>
</tr>
<tr>
<td>4</td>
<td>Hexaferrite</td>
<td>6 Fe₂O₃ – 1MeO</td>
<td>MeO is a divalent metal oxide from group IIA e.g. BaO, CaO, SrO</td>
</tr>
</tbody>
</table>

(i) Spinel: Ferrites with the formula AB₂O₄, constitute the first group of ferrites, where A and B represent various metal cations like iron. Spinel ferrites are magnetically soft and they are alternative to metallic magnets such as Fe and layered Fe-Si alloys, but exhibit enhanced performance due to their outstanding magnetic
properties [6, 7]. Spinel ferrites have the properties such as high electrical resistivity and low magnetic losses. The two popular ceramic magnets; Nickel-Zinc ferrites and Manganese-Zinc ferrites are the major members of the spinel ferrite family. They have been intriguing ceramic materials due to their high electrical resistivity, high magnetic permeability and possible modification of intrinsic properties over a wide spectrum [1].

(ii) Garnet: The second group of ferrites is the garnet type ferrites. Garnets, unique magnetic ceramics have optical transparency and used in magneto-optical applications [8]. Yttrium iron garnet (YIG) is a synthetic garnet with chemical composition Y$_3$Fe$_5$O$_{12}$. Yttrium can be replaced by one of the rare earth ions like La$^{3+}$, Dy$^{3+}$, Gd$^{3+}$, Er$^{3+}$, etc. with an atomic number greater than 61.

(iii) Ortho ferrites: Ortho ferrites possess extremely high velocities of the domain wall motion and it is used in communication techniques, in optical internet, in sensors of magnetic fields and electrical currents, mechanical quantities etc.

(iv) Hexagonal ferrites: In 1952, a new class of ferrites having permanent magnetic properties was discovered. Workers at Philips laboratory at Eindhoven in the Netherlands made the developments of hexagonal ferrites possible. Hexagonal ferrites (general formula MFe$_{12}$O$_{19}$ where M is usually Barium Ba, Strontium Sr, Calcium Ca or Lead Pb) have been distinguished due to their high uniaxial magneto-crystalline anisotropy which renders them perfect for permanent (hard) magnet applications [9]. The crystal structure of hexaferrite is complex but it can be described as hexagonal with a unique c axis, which is the easy axis of magnetization in the basic structure. Hexagonal ferrites are referred to as hard as the direction of magnetization cannot be changed easily to another axis. Barium ferrite (BaFe$_{12}$O$_{19}$) and Strontium ferrite (SrFe$_{12}$O$_{19}$) are the examples of hexagonal ferrites and they have received much interest in recent years because of microwave device applications. Barium hexaferrite is especially of interest for use in hybrid microwave devices, monolithic microwave integrated circuits or even as a future replacement for yttrium iron garnet [10] due to its high uniaxial anisotropy and large resistivity. The next generation of magnetic microwave devices (isolators, filters, phase shifters, and circulators and
related components) will be planar, self-biased, and low loss, and operate better than today’s devices [11].

Hexaferrites are subclassified into six subclasses namely; M, W, Y, Z, X and U type according to their crystal structure and arrangement of respective S, R and T blocks. Table 1.2 shows the subclasses of Hexaferrite with their chemical formulae. Where, A represents Ba, Pb or Sr and Me is a divalent transition metal ion.

Table 1. Subclasses of Hexaferrites.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Hexaferrite type</th>
<th>Chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M-type</td>
<td>AFe₁₂O₁₉</td>
</tr>
<tr>
<td>2</td>
<td>Y-type</td>
<td>A₂Me₂Fe₁₂O₂₂</td>
</tr>
<tr>
<td>3</td>
<td>W-type</td>
<td>AMe₂Fe₁₆O₂₇</td>
</tr>
<tr>
<td>4</td>
<td>X-type</td>
<td>A₂Me₂Fe₂₈O₄₆</td>
</tr>
<tr>
<td>5</td>
<td>U-type</td>
<td>A₄Me₂Fe₃₆O₆₀</td>
</tr>
<tr>
<td>6</td>
<td>Z-type</td>
<td>A₃Me₂Fe₂₄O₄₁</td>
</tr>
</tbody>
</table>

The crystal structure of these different types of hexaferrite is complex and can be considered as a superposition of S, R and T blocks along the hexagonal c-axis. S block represents a spinel block which consists two oxygen layer (O₄-O₄) with composition Fe₆O₈. R is a three oxygen layer block (O₄-BaO₃-O₄) with composition BaFe₆O₁₁. T is a block of four layers of oxygen ions (O₄-BaO₃-BaO₃-O₄) with composition Ba₂Fe₈O₁₄. Astrik (*) shows that the corresponding block is rotated 180° around the hexagonal c-axis [12].

1.3 Applications of hexaferrites

M-type hexaferrites have continuously made inroads in applications such as plastoferrites, injection-molded pieces, microwave devices, and magnetic recording media. With proper design and substitutions, passive elements including mm-wave circulators can be constructed from hexaferrites. Hexaferrite with proper design and substitution are used as passive elements at microwave frequencies [13]. Radar absorbing paint made from ferrites is used to coat military aircrafts for stealth.
operation and in the expensive absorption tiles lining the rooms used for electromagnetic compatibility measurements.

Other applications of hexaferrite materials include Common Mode Chokes, EMI filters, Current Sensors, Handheld Devices, Spike Suppression and Gate Drive Transformers, shield beads, snap-on cores, flat cable beads (Figure 1.1), automotive industry and consumer goods [14].

![Figure 1.1 Hexaferrites as different beads in data cables](image)

Hexaferrites having the intrinsic characteristics of Complex Permeability ($\mu'$ & $\mu''$) and High Impedance, they are also used in

(i) Computers and peripherals  
(ii) Communication Systems  
(iii) Automobiles  
(iv) Switch Mode Power Supplies  
(v) dc-dc converters  
(vi) Ignition coils

### 1.4 Literature Survey

In order to prepare ferrites with better qualifications, precipitation and heat treatment techniques were first performed by Forestier in 1928 [6]. The major contributions to reveal the physics operating in ferrites were achieved both by the researchers conducted in Japan by V. Kato et. al. From 1932 to 1935 and the studies carried out by Snoek et. al. at Philips Laboratories in the Netherlands between 1936 and 1945 [6, 15]. Finally in 1945, the basic physics and technology of practical ferrite materials were described by Snoek who initiated and pursued the development of ferrites into useful materials [8]. The major booming of the ferrite industry was led by the large-scale introduction of television in the 1950s. In television sets, ferrite cores
were used as high-voltage transformers and electron beam deflection yokes due to their strong magnetic properties, high electrical resistivity and low magnetic losses. In 1959, J. Smit and H. P. J. Wijn published a comprehensive book on ferrites. Since then developments have been made on the magnetic characteristics of ferrite materials that have improved device performances. These involve both compositional and processing modifications in addition to improvements succeeded in device design. A very wide range of Curie points, remanent magnetization, saturation magnetization and coercive fields have been obtained due to wide range of substitutional solid solution that makes it possible to tailor the magnetic properties of polycrystalline magnetic ceramics. Thus, ceramic magnets are molecularly designed and processed for specific electronic applications \[15, 16\].

The Murray group at the IBM Watson [17-19] research centre has studied the synthesis of mono disperse metallic magnetic nanoparticles intensively. They have synthesized cobalt nanoparticles with several different crystal structures using different synthetic procedures. Relatively very little work has been done to synthesize uniform iron nanoparticles. Suslick et al. reported the synthesis of iron nanoparticles from the sono-chemical decomposition of iron penta carbonyl in the presence of poly vinyl pyrrolidone (PVP) or oleic acid [20]. Major drawback of the sono-chemical process in the synthesis of nanoparticles is its inability to control particle size.

Mn-Zn-ferrites were prepared by using a Microemulsion and reverse Microemulsion techniques by the group of A. Košak. They observed that the surfactant/oil ratio as well as pH of the reaction affects the particle size and morphology of the product [21, 22]. S. Alamolhoda [23] has intensively studied the formation of strontium hexaferrite nanopowder by a sol -gel auto-combustion method in the presence of surfactant CTAB. They show the results that surfactant addition to the gel makes the particle size of the final product much smaller (35-40 nm).

Microstructure, hysteresis and microwave absorption properties of $\text{Ba}_{(1-x)}\text{Sr}_x\text{Fe}_{12}\text{O}_{19}$ ferrite was investigated by S. Bindra Narang et. al.[24]. The results show with increasing value of $x = 0.0$ to 1.0 causes reduction in Curie temperature from 441 to 393 °C. Microwave absorption properties of $\text{SrFe}_{12}\text{O}_{19} /\text{ZnFe}_2\text{O}_4$ composite powders were investigated by Na Chen et. al.[25].
They observed that the additions of ZnFe$_2$O$_4$ make the minimum reflection loss frequency of the composite powders shift to a higher frequency than that of pure strontium ferrite. The improvement of absorption performance may be attributed to relative permeability change induced by exchange coupling interaction between hard magnetic and soft magnetic materials. Debangsu Roy and P. S. Anil Kumar presented the enhancement of $(BH)_{\text{max}}$ by $\sim 13\%$ in a hard-soft-ferrite nanocomposite using exchange spring mechanism [26].

J. F. Wang et. al. [27] reported a preparation of ultrafine Sr-M particles with high coercivity, 6635 Oe using a co-precipitation method and the effect of Sm$^{3+}$/Sr$^{2+}$ ratio on the magnetic properties of Sm doped Sr-M particles was studied. M. M. Hessien group has used Hydrogen reduction process to enhance the magnetic properties of Barium hexaferrite through ceramic route [28]. In 1997, H. Yamamoto group have investigated the magnetic properties of mono phase Sr-M fine particles (~200 nm) prepared at lower sintering temperature by a co-precipitation method [29].

Balwinder Kaur et. al. reported the modifications in magnetic anisotropy of M-type Strontium hexaferrite crystals by the swift heavy ion irradiation of 50 MeV Li$^{3+}$ ions [30]. They studied the effect of 50 MeV Li$^{3+}$ ion irradiation on mechanical characteristics of pure and Ga-In substituted M-type Strontium hexaferrite [31]. The Influence of 85 MeV oxygen ion irradiation on magnetization behavior of micron-sized and nano-sized powders of SrFe$_{12}$O$_{19}$ had been studied by Shinde and group. The results revealed that there is a significant change in hysteresis loop features observed after irradiation in the case of micron-sized powders, whereas no change is seen in the case of nano-sized powders [32]. Only few researchers have studied the irradiation effect on ferrites with lower energetic ions such as Li, O etc. No work has been done on the irradiation with Ag$^{16+}$ ions on Strontium hexaferrites yet.

1.5 Aim of the present work

Hexaferrites and their composites has been the subject of an extensive study because of their wide range of technical applications and their importance in understanding the theories of magnetism. They exhibit interesting microstructural, electrical and magnetic properties which depend upon various parameters like method of preparation, calcinations temperature, preparation time, amount of substitution,
types and amount of surfactant etc. In recent years, chemical co-precipitation technique is used to prepare hexaferrites. Literature survey reveals that co-precipitation technique is a versatile low-cost technique to obtain ultrafine, homogeneous hexaferrite particles; while micro emulsion and the self propagating high temperature synthesis techniques are used to prepare nanosized hexaferrite particles.

The aim of present work is multi fold:

(i) To synthesize M-type SrFe$_{12}$O$_{19}$ hexaferrite particles, using three different techniques namely; a co-precipitation, a microemulsion and a self propagating high temperature synthesis (SHS) and to compare thermal, microstructural, magnetic and dielectric properties.

(ii) To investigate effect of different temperature and surfactants on formation of Sr-hexaferrite particles in order to find best sintering temperature and surfactant.

(iii) One of the major aspect of the present work is preparation of magnetically tailored, mono phase nano sized particles at relatively low sintering temperature using surfactants.

(iv) To prepare composites of SrFe$_{12}$O$_{19}$ and CoFe$_2$O$_4$ using SHS route in order to improve dielectric and magnetic properties.

(v) To study the effect of swift heavy ions irradiation on synthesized SrFe$_{12}$O$_{19}$ hexaferrite particles.
References


