Chapter One

Introduction

Ferrites or ferromagnetic 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 [1]. The magnetic behavior exhibited by the ferrites is quite different from ferromagnetism that is exhibited by metallic materials. Ferrites are also non-conducting magnetic media, so eddy current and holmic losses are less than for ferromagnetic materials .They are the common in nature and are often used as transformer cores at radio frequencies (RF). From the daily iron oxide, magnetite (Fe_3O_4) formed at the surface of many iron-containing objects like fences, cars, doors, barbecue grills. Ferrite exhibits ferromagnetism 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 [1]. 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 sub-lattices.

The basic theory of spin-spin interaction in ferrites was developed by Neel [2] in 1948, who introduced the idea of magnetic sub lattice. A more detailed examination of the basic interaction of the spin system was made by Anderson [3] in 1951 and Van-Vleck [4].

Yafet and Kittle [5] in 1952, extended the theory of magnetic sub lattice by postulating a triangular arrangement of the three sub lattice, when antiferromagnetic exchange interactions between sub lattice is comparable to that among the spin moments within the sub lattice formed by Fe^{3+} ions on tetrahedral and octahedral sites.

1. Classification of ferrites

Ferrites are often classified according to their magnetic properties as "soft" and "hard" ferrites, which refer to their low or high coercivity of their magnetism, respectively. However, they could also be classified according to their crystal structure [1].In material the coercivity also called coercive felid or coercive force, is measure of ferromagnetic or ferroelectric material to withstand an external magnetic or electric filed [5].

1.1 Classification based on magnetic properties

1.1.1 Soft ferrites

Soft ferrites are ferromagnetic materials with cubic crystal structure and they are characterized by chemical formula $MO{\cdot}Fe_2O_3$, 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 [6].

1.1.2 Hard ferrites

Permanent ferrite magnets are made up of hard ferrites, which have a high coercivity 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 $BaO{\cdot}6Fe_2O_3$ and $SrO{\cdot}6Fe_2O_3$, but Sr-M hexaferrite has slightly superior magnetic properties [6].

1.2 Classification according to crystal structure

The ferrites consist dominant compound of Fe_2O_3, are divided into four groups namely Spinal, Garnet, Ortho and Hexagonal ferrites. These ferrites are distinguished with respect to the molar ratio of Fe_2O_3 to other oxide components present in the ceramic as shown in Table 1.1.

Table 1.1: Classification of ferrites based on crystal structure, [6]

No.	Types	Molar ratio	Representations
1	Spinel	Fe_2O_3.1MO	MO is a transition metal oxide
2	Garnet	5 Fe_2O_3.3 M_2O_3	M_2O_3 is a rare earth metal oxide
3	Ortho	$AFeO_3$	A is rare earth elements, e.g. Ho, Dy, Er, Y, Yb
4	Hexaferrite	6 Fe_2O_3.1MO	MO is a divalent metal oxide from group IIA e.g. BaO, CaO, SrO

1.2.1 Spinel ferrites

Ferrites with the formula AB_2O_4, 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 [7, 8].

1.2.2 Garnet ferrites

The second group of ferrites is the garnet type ferrites. These ferrites are unique magnetic ceramics and have optical transparency and are used in magneto-optical applications [9].

1.2.3 Ortho ferrites

Ortho ferrites possess extremely high velocities of the domain wall motion and it is used in communication techniques, optical internet, sensors of magnetic fields and electrical currents, mechanical quantities etc [9].

1.2.4 Hexagonal ferrites of alkaline earth metal

In 1952, a new classified of Hexagonal ferrites having permanent magnetic properties was discovered [5].Workers at Philips laboratory at Eindhoven in the Netherlands made the developments of hexagonal ferrites possible. Hexagonal ferrites are of the general formula $MFe_{12}O_{19}$ (where M is usually Ba, Sr, Ca or Pb) have been distinguished due to their high uni-axial magneto-crystalline anisotropy, which renders them perfect for permanent (hard) magnet applications [10]. 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 due to its high uniaxial anisotropy and large resistivity[11]. The next generation of magnetic microwave devices (isolators, filters, phase shifters, and circulators and related components) will be planar, self-biased, low loss and operate better than today's devices [12]. Hexaferrites are sub classified 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 [12].

Table 1.2 shows the subclasses of Hexaferrite with their chemical formulae. In all chemical formulas of these subclasses of ferrites, A represents Ba, Pb or Sr, where M is a divalent transition metal ion.

Table 1.2: Subclasses of Hexaferrites [12]

No.	Hexaferrite type	Chemical formula
1	M-type	$AFe_{12}O_{19}$
2	Y-type	$A_2M_2Fe_{12}O_{22}$
3	W-type	$AM_2Fe_{16}O_{27}$
4	X-type	$A_2M_2Fe_{28}O_{46}$
5	U-type	$A4M_2Fe_{36}O_{60}$
6	Z-type	$A_3M_2Fe_{24}O_{41}$

1.3 Alkali metal ferrites

Alkali metal ferrites are ferromagnetic oxide materials exhibiting high magnetization, Curie temperature and low eddy current losses. These materials are extensively used in high capacity batteries, intercalation electrodes in rechargeable batteries, strong oxidizing agents, and audio-video digital recording and low magnetization Ferro fluids [13, 14].

1.4 Literature Survey

The credit of first scientific research on magnetic materials goes to William Gilbert. In 1600, he wrote a book in which he discussed the magnetic behavior of different materials and also diverted the attention towards magnetism retained by planet earth [6]. After the passing of two hundred years, Hans Christian Oersted in 1800, observed the presence of magnetic field around a current carrying conductor and provided a foundation for electromagnetism [6]. Later on, Ampere, Faraday, Curie, Maxwell etc. contributed their research for the development of electromagnetic theory [1]. However, in 1930's, formal research on soft ferrites was started in Japan and Netherland. Since then it is on its way [1].

Over the last few decades the interest towards soft magnetic materials has substantially increased due to increasing demand for improved performances of electromagnetic gadgets, memory or data storage devices, sensors etc.[6]. Oxide based soft magnetic ferrite are one of the major contenders in this field of application [6].

Now a days, it is mainly focused on the development of innovative synthesis routes to prepare ferrite compositions such as MFe_2O_4 (where M=Mg, Zn, Ni, Mn, Ba or combination of these) at nanoscale [7]. The electromagnetic properties of synthesized compositions are being tailored with addition/substitution of transition metal oxides [7].

Consequently, the properties of magnetically disorder ferrites have remained a subject of considerable interest for the last few decades [15].

Precursor methods are simple, inexpensive, do not require elaborate experimental setup and is less time consuming. The ferrites prepared by this method are found to exhibit better properties than those prepared by ceramic method [16].

Koop [17] in 1951, gave the theory of low frequency dispersion by assuming that polycrystalline sintered ferrites consist of large domains of well conducting grains separated by relatively thin poor conducting layers producing interfacial polarization of Maxwell- Wagner type.

The conventional ceramic method, i.e. solid state reaction technique, involves milling of the reactants followed by heating at elevated temperature range. Whereas, the non-conventional process involves producing powdered material through a wet chemical method. Auzans and co-workers [18] used co-precipitation method for the synthesis of ferrites. Various material preparation methods such as hydrothermal precipitation process Sol-gel synthesis and the micro-emulsions approach have been often used to synthesize the Mn-Mg ferrite materials [19].

Porosity at the grain boundaries and within the grain causes hindrance to the domain wall motion and is damaging to the initial permeability [20]. Particle size significantly affects the magnetic properties of ferrites. Tang et al [21] observed the changes in saturation magnetization with particle size. Rezlescu and Rezlescu [22] studied the composition, frequency and temperature dependence of copper containing mixed ferrites such as copper manganese ferrites and copper zinc ferrites.

In 1959, Smit and 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, remnant magnetization, saturation magnetization and coercive fields have been obtained due to wide range of substitution 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 [22, 23]. Xian- Ming Liu etal [24] have synthesized Mn-Zn ferrites by precursor method.

In 1959, Smit and 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, remnant magnetization, saturation magnetization and coercive fields have been obtained due to wide range of substitution 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 [25].

Daun and co-workers [26, 27] have designed novel synthesis route of pure MFe_2O_4 (M=Mg, Co, Ni) spinel ferrites using a single molecular precursor. Among these methods of preparation, the precursor method of the synthesis of inorganic solid has attracted the attention of solid state chemists for the fact that the product formed is of high purity and homogeneity on an atomic scale in precursor itself thereby decreasing their diffusion distance of reactive cations during the formation of the product and thus lowering the temperature of formation.

Solid solution precursor technique has been used to prepare fine particle ferrites MFe_2O_4, where M= Mg, Mn, Co, Ni, and Zn [28], and Ni-Zn ferrites [28] which were sintered at low temperature to give dense ferrites. Powdery nickel ferrite, $NiFe_2O_4$ has been obtained by soft mechano-chemical synthesis in a planetary ball mill. $Ni(OH)_2$ and $Fe(OH)_3$ are used as initial compounds. This mixture was mechanically

activated for 25 h, uniaxial pressed and sintered at 1100 °C for 2 h [29].

Chapter Two

Experimental

2.1 Materials and Equipment

The following materials, glassware and instruments were used for the synthesis of the targeted ferrite materials:

- Ferrous sulfate heptahydrate, $FeSO_4.7H_2O$, Minimum assay98%, Prabhat chemicals.
- Potassium nitrate KNO_3, Minimum assay, 87%, Industry Scott scienc, UK.
- Potassium hydroxide KOH, Minimum assay 85%, Industry Scott scienc, UK.
- Hydrochloric acid HCl, Density1.18g cm^{-3}, Minimum assay 35 - 38 %, Lobachemie.Pvt. Ltd. India.
- Barium chlorides BaCl2, Minimum assay 96 % Prabhat chemicals.
- Ammoniumoxalates monohydrate $(NH_4)_2C_2O_4.H_2O$, Minimum assay97% Prabhat chemicals.
- Magnesium sulphateheptahydrate $MgSo_4.7H_2O$, Assay 97%,CDH, India
- Calcium Chloride anhydrous $CaCl_2$, assay79.9% CDH, India
- Strontium chloride hexa hydrate ($SrCl_2.6H_2O$), Assay 98%,CDH, India.
- Hot plate stirrer (Model, origin) and Muffle furnace (Model, origin).

2.2 Synthesis of ferrites

2.2.1 Iron ferrite (Fe-Fer)

27.8 g of hydrated ferrous sulfate ($FeSO_4.7H_2O$) were dissolved in 200 mL of distilled water in a beaker. In another beaker, 2.00 g of sodium nitrate (KNO_3) and 15 g of potassium hydroxide (KOH) were dissolved in 100 mL of distilled water. Each solution was heated to about 75 °C then mixed together with vigorous stirring. A thick gelatinous green precipitate was formed. After being stirred at 90 - 100°C for 10 min, the precipitate turned to finely divided dense black substance. The mixture was cooled to room temperature and was made acidic with few drops of 6M HCl. The precipitate was filtered through normal filter paper and washed with distilled water until the wash water had given no test for sulfate with barium chloride ($BaCl_2$) solution. The material was dried at 110°C for 2 hours and weighed [31].

2.2.2 Magnesium Ferrite (Mg-Fer)

A mixture of 7.315 g of Magnesium sulfate hepta hydrate ($MgSO_4.7H_2O$), 9.27 g of hydrated ferrous sulfate ($FeSO_4.7H_2O$) and 0.6 mL of sulfuric acid (10% H_2SO_4) were dissolved in 66.6 mL of distilled water in a beaker. In another beaker 7.33 g of Ammonium oxalate mono hydrate $(NH_4)_2C_2O_4.H_2O$ were dissolved in 100 mL of warm distilled water. Each solution was heated to about 75 °C then mixed together with vigorous stirring. Then oxalate solution was added to the

metal sulfate solution. A thick yellow gelatinous precipitate was formed. After being stirred at 90 - 100°C for 5 min, the mixture was cooled to room temperature and was made acidic with few drops of 6M HCl.

The precipitate was filtered through normal filter paper and washed with distilled water until the wash water had given no test for sulfate with barium chloride ($BaCl_2$) solution. The as-synthesized material was dried at 110 □C for 2 hours then calcined at about 700°C for 3 hours and weighed [31].

2.2.3 Calcium Ferrite (Ca-Fer)

A mixture of 4.91 g of Calcium Chloride ($CaCl_2$), 13.9 g hydrated ferrous sulfate ($FeSO_4.7H_2O$) and 1 mL of sulfuric acid (10% $H_2SO_{4)}$ was dissolved in 100 mL of distilled water in a beaker. In another beaker 11.0 g of ammonium oxalate mono hydrate $(NH_4)_2C_2O_4.H_2O$ were dissolved in 150 mL of warm distilled water. Each solution was heated to about 75 °C then mixed together with vigorous stirring. Then oxalate solution was added to the metal sulfate solution. A thick yellow gelatinous precipitate was formed. After being stirred at 90 - 100°C for 5 min, the mixture was cooled to room temperature and was made acidic with few drops of 6M HCl. The precipitate was filtered through normal filter paper and washed with distilled water until the wash water had given no test for sulfate with barium chloride ($BaCl_2$)

solution. The as-synthesized material was dried at 110 □C for 2 hours then calcined at about 700°C for 3 hours and weighed [31].

2.2.4 Strontium Ferrite (Sr-Fer)

A mixture of 11.89 g of Strontium chloride hexa hydrate ($SrCl_2.6H_2O$), 13.9 g of hydrated ferrous sulfate ($FeSO_4.7H_2O$) and 1 mL of sulfuric acid (10% $H_2SO_{4)}$ were dissolved in100 mL of distilled water in a beaker. In another beaker 11.0 g of ammonium oxalate hydrate $(NH_4)_2C_2O_4.H_2O$ were dissolved in 150 ml of warm distilled water. Each solution was heated to about 75 °C then mixed together with vigorous stirring. Then oxalate solution was added to the metal sulfate solution. A thick Yellow gelatinous precipitate was formed. After being stirred at 90 - 100°C for 5 min, the mixture was cooled to room temperature and was made acidic with few drops of 6M HCl. The precipitate was filtered through normal filter paper and washed with distilled water until the wash water had given no test for sulfate with barium chloride ($BaCl_2$) solution. The material was dried at 110 □C for 2 hours then calcined at about 700°C for 3 hours and weighed [31].

2.2.5 BariumFerrite (Ba-Fer)

A mixture of9.292 g of Barium chloride ($BaCl_2$), 13.9 g of hydrated ferrous sulfate ($FeSO_4.7H_2O$) and 1 mL of sulfuric acid (10% H_2SO_4)were dissolved in100 mL of distilled water in a beaker. In

another beaker 11.0 g of ammonium oxalate mono hydrate $(NH_4)_2C_2O_4.H_2O$ were dissolved in 150 mL of warm distilled water. Each solution was heated to about 75 °C then mixed together with vigorous stirring. Then oxalate solution was added to the metal sulfate solution. A thick Yellow gelatinous precipitate was formed. After being stirred at 90 °C to 100°C for 5 min, the mixture was cooled to room temperature and was made acidic with few drops of 6M HCl. The precipitate was filtered through normal filter paper and washed with distilled water until the wash water had given no test for sulfate with barium chloride ($BaCl_2$) solution. The material was dried at 110 □C for 2 hours then calcined at about 700°C for 3 hours and weighed [31].

2.3 Characterization Methods

2.3.1 Fourier Transform Infra-Red spectroscopy

Fourier Transform Infra-Red (FT-IR) data of (Mg-Fer), (Ca-Fer), (Sr-Fer), (Ba-Fer) and (Fe-Fer) were obtained using (Shimadzu, Japan) 8400S FT-IR spectrometer in the wave number range of 400-4000 cm^{-1}, with KBr discs. The KBr disk was prepared at weight ratio of KBr (spectral grade) to ferrite samples of about 20:1.

2.3.2 X-Ray Diffraction (XRD)

The powder X-ray diffraction patterns of the ferrite samples were collected from Philips PW 3719 (Voltage of 40 kV and current of 30 mA)

using CuKα. (λ = 0.154 nm) radiation. The diffraction angle was scanned in the 2θ range from 5° to 70° for 2h, at a rate of 6°/ min.

2.3.3Atomic absorption spectroscopy

An atomic absorption spectroscopic (AAS) analysis was conducted for the aqueous solutions of ferrite samples using Varian model spectra (220 FS) equipped with acetylene-air mixture as carrier gas. The aqueous solution of any ferrite sample was obtained by digesting about 1 g of solid sample in a little quantity of concentrated hydrochloric acid. The resultant acidic solution was diluted to 100 mL with distilled water.

Chapter Three

Results and discussion

3.1 Yields of synthesized ferrites

Different ferrites were synthesized from hydrated Iron (II) sulphate and salts of alkaline earth metal cations using established methods [6] as described in the experimental part. These ferrites are

Iron ferrite(Fe-Fer), Magnesium Ferrite (Mg-Fer), calcium Ferrite (Ca-Fer), Strontium Ferrite (Sr-Fer) and BariumFerrite (Ba-Fer).The appearances and yields of the produced ferrites are illustrated in Table 3.1. As shown in Table 3.1, with exception of Fe-Fer, the colors of these ferrites are similar and resemble those reported in the literature [6]. Fe-Fer characterized with dark black color which also resembles the color of commercial Fe-Fer [6]. The yields percentages of these ferrites, however, were found to be different. Fe-Fer and Mg-Fer samples exhibited lower percentages of yields, whereas higher yields percentages were registered for Ba-Fer and Ca-Fer.

Table 3.1: The yields of as-synthesized ferrites

No.:	Samples	Appearance	Weight (g)	%
1	Iron ferrite or Magnetite (Fe-Fer)	Black powder	7.12	25.6
2	Magnesium Ferrite (Mg-Fer)	Brown powder	2.20	30.1
3	Calcium Ferrite (Ca-Fer)	Brown powder	4.21	85.7
4	Strontium Ferrite (Sr-Fer)	Brown powder	8.19	68.9
5	Barium Ferrite (Ba-Fer)	Brown powder	9.29	90.7

3.2 Fourier Transform Infra-Red of Ferrites

Figure 3.2.1 shows the FT-IR spectrum of Mg-Fer in the range of 400-4000 cm^{-1}.The bands at 3732 cm^{-1} and 3622 $cm^{-1}$are due to O-H stretching vibration of physi- absorbed water.The peak at 2363 cm^{-1} is due to O=C=O of atmospheric CO_2, whereas the peak at 1518 cm^{-1} is

assigned to O-H bending vibration of physically adsorbed water. Many peaks assigned to M-O bonds were observed in therange of 1000- 400 cm^{-1}. The peak at 560 $cm^{-1}$is due toMg-O bond of calcined Mg-Fersample, whereas the band at 450-385 cm^{-1}strongly suggests the intrinsic stretching vibrations of the iron (Fe-O) at the tetrahedral site [32-34].

Figure 3.2.1: The FT-IR spectrum of synthesized Magnesium Ferrite material (Mg-Fer)

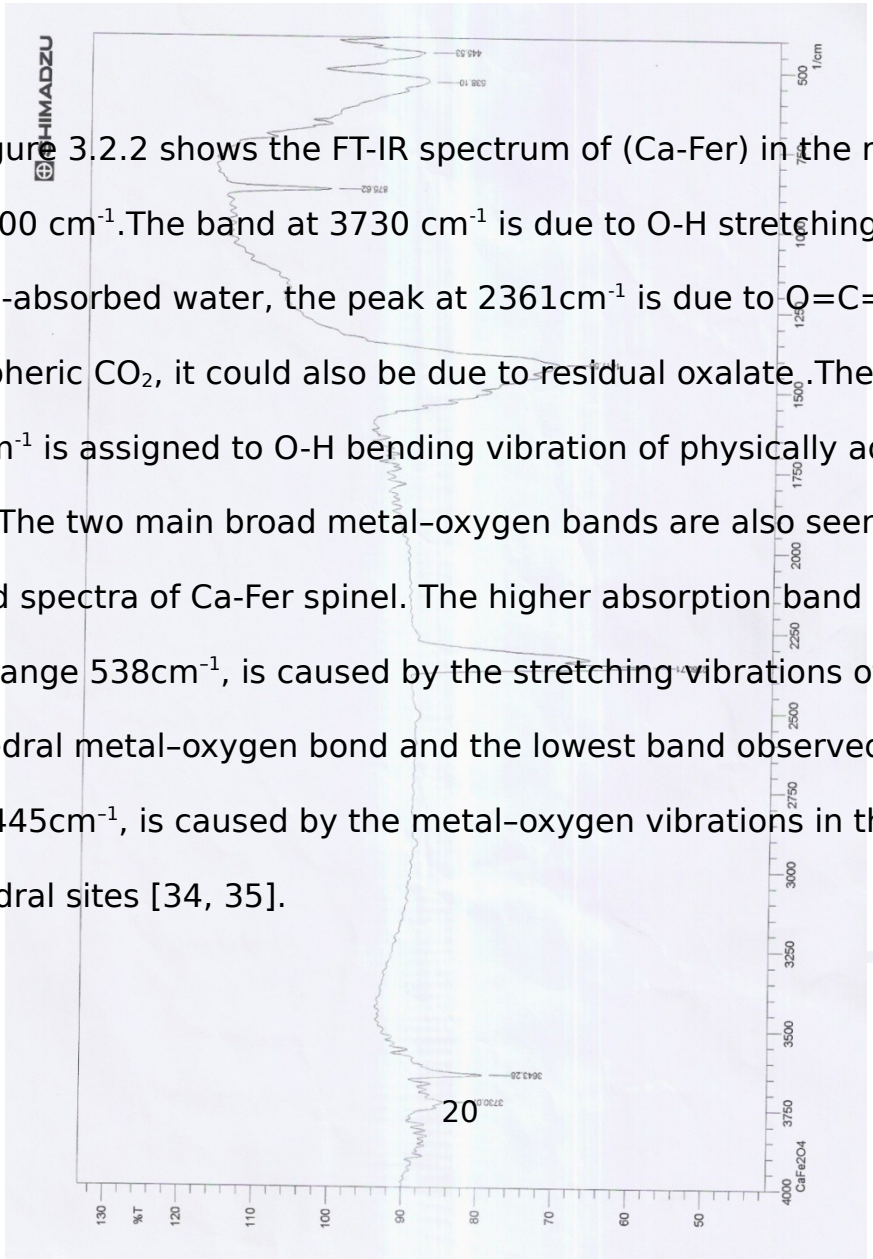


Figure 3.2.2 shows the FT-IR spectrum of (Ca-Fer) in the range of 400-4000 cm^{-1}.The band at 3730 cm^{-1} is due to O-H stretching vibration of phys-absorbed water, the peak at 2361cm^{-1} is due to O=C=O of atmospheric CO_2, it could also be due to residual oxalate .The band at 1418cm^{-1} is assigned to O-H bending vibration of physically adsorbed Water. The two main broad metal–oxygen bands are also seen .In infrared spectra of Ca-Fer spinel. The higher absorption band observed in the range 538cm^{-1}, is caused by the stretching vibrations of the tetrahedral metal–oxygen bond and the lowest band observed in the range 445cm^{-1}, is caused by the metal–oxygen vibrations in the octahedral sites [34, 35].

Figure 3.2.2: The FT-IR spectrum of synthesized Calcium ferrite material (Ca-Fer)

Figure 3.2.3 shows the FT-IR spectrum of ($BaFe_2O_4$) in the range of 400-4000 cm^{-1}.The band at 2359-2343$cm^{-1}$is due to O=C=O of atmospheric CO_2, it could also be due to residual oxalate that were embedded in the powder material. The band at 1418 cm^{-1} is assigned to O-H bending vibration of physically adsorbed water..the peaks at 1193.85 cm^{-1}, 1114.78 cm ,1076.82 cm^{-1} and shoulder peak at 983.63 cm^{-1}due to vibrations absorptions sulfate (S=O)due to in complete the reaction in preparation . The main metal–oxygen bands are also seen the main metal–oxygen bands are also seen. The higher absorption band observed in the range in the range 600–550 cm^{-1} is caused by the

stretching vibrations of the tetrahedral M–O bond and the lowest band observed in the range 450–385 cm^{-1}, is caused by the M-O vibrations in the octahedral sites [34, 36]

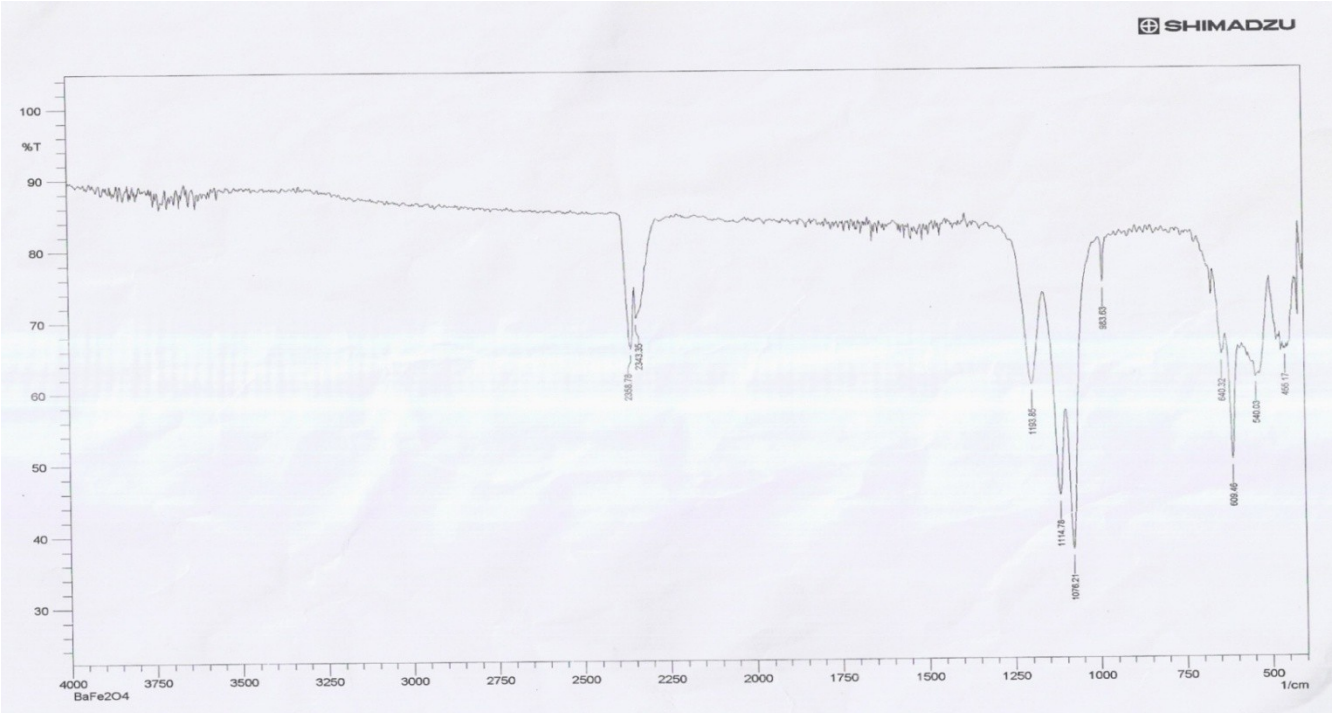


Figure 3.2.3: The FT-IR spectrum of synthesized Barium Ferrite material (Ba-Fer)

Figure 3.2.4 shows the FT-IR spectrum of Strontium Ferrite (Sr-Fer) in the range of 400-4000 cm^{-1},The band at 3742 cm^{-1} is due to O-H stretching vibration of physi-absorbed water, the peak at 2361 - 2336 cm^{-1} is due to O=C=O of atmospheric CO_2. The peak at 1699 cm^{-1} and peak at 1516 cm^{-1}due to O-H is assigned to O-H bending vibration of physically adsorbed water. The peak appears at1465 cm^{-1} due to absorption of strontium carbonate bands [34, 33]. The main

metal–oxygen bands are also seen. The higher absorption band observed in the range of 550–580 cm^{-1}, is caused by the stretching vibrations of the tetrahedral M–O bond and the lowest band observed in the range 430–470 cm^{-1}, is caused by the M–O is vibrations in the octahedral sites [36, 37].

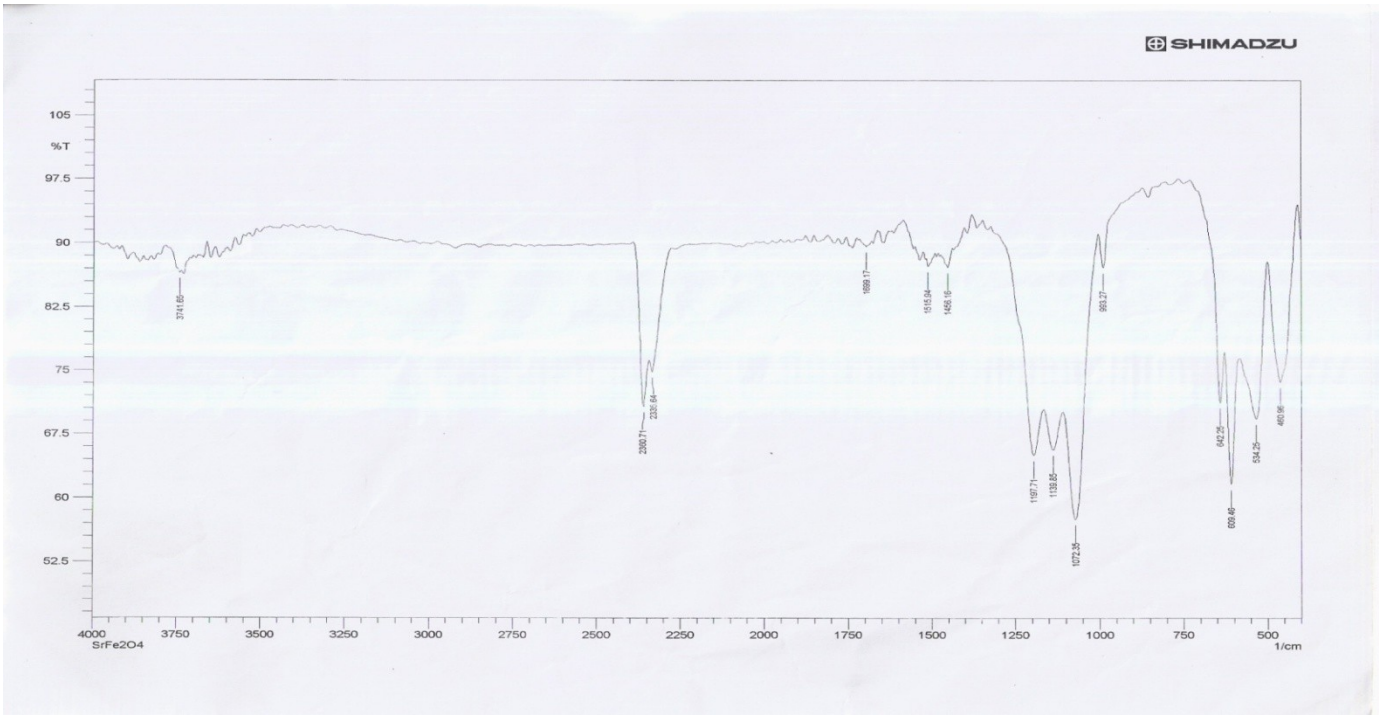


Figure 3.2.4: The FT-IR spectrum of synthesized Strontium Ferrite material (Sr-Fer)

Figure 3.2.5 shows the FT-IR spectrum of Iron Ferrite (Fe-Fer) in the range of 400-4000 cm^{-1}.The band at 3736 cm^{-1} is due to O-H stretching vibration of physi-absorbed water. The band at1531cm^{-1} is assigned to O-H bending vibration of adsorbed water. The peak at 2359 cm^{-1} is due to O=C=O (from adsorbed carbon dioxide) , the characteristic peak at

567 cm^{-1} is due to Fe–O band that matches well with the characteristic peak of Fe_3O_4 [38].

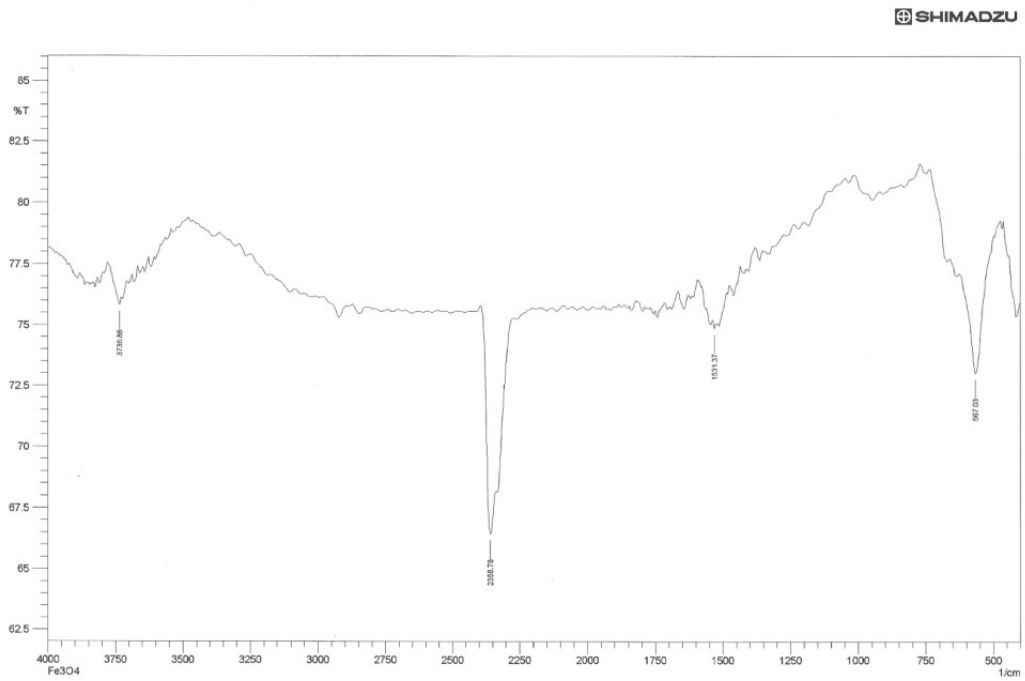


Figure 3.2.5: The FT-IR spectrum of synthesized Iron Ferrite material (Fe-Fer)

3.3 X-ray Diffraction analysis

The crystallite size of Mg-Fer is shown in Figure 3.3.1. The investigated solids was based on X-ray diffraction line broadening and calculated by using Scherer equation [39]. D= 0.89K/ (β cosθ), the sample consisted entirely of magnesium ferrite, Mg-ferr (JCPDS card No. 17- 464) with different planes (111), (220), (311), (400), (422), (511) and (440) with respective 2θ angles of 18.507□, 30.448□, 35.868□, 43.599□, 54.107□, 57.686□, 63.361□ of cubic spinel structure.

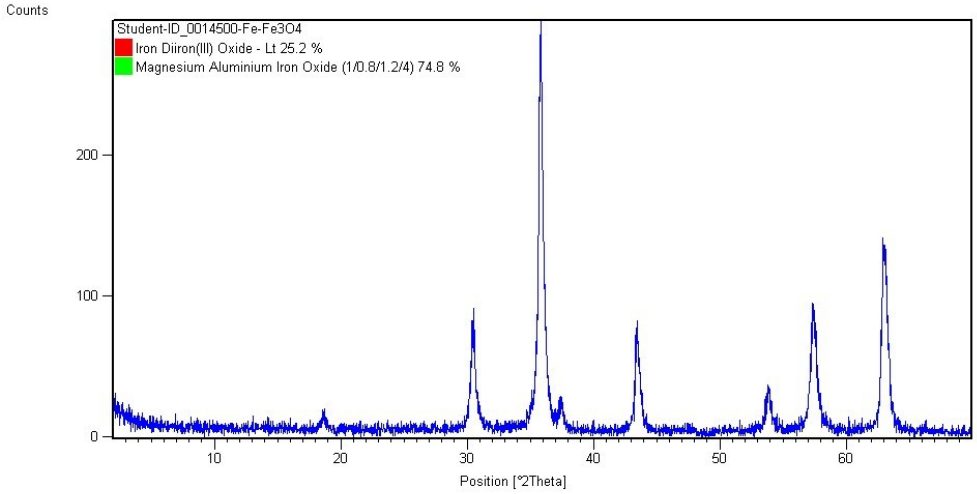


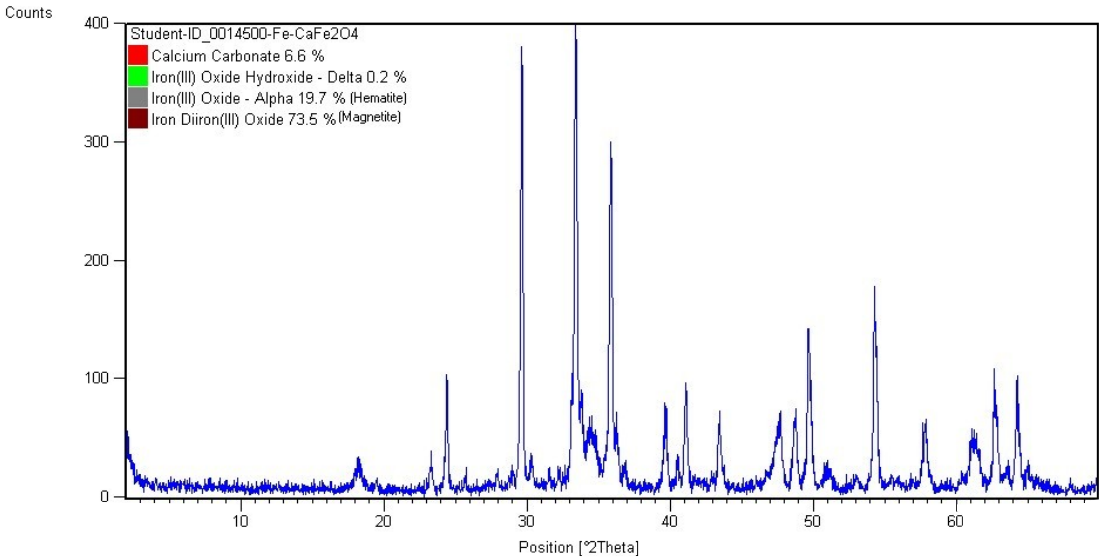
Figure 3.3.1: The XRD diffraction pattern of the synthesized Magnesium Ferrite (Mg-Fer)

As is already known, the distribution of cations between tetrahedral, and octahedral sites included in the spinel structure and are more sensitive to the change in the intensities of the (220) and (440) planes, respectively [40]. However, the intensities of the (511) plane is sensitive to the change in oxygen ion parameters [40]. Indeed, the Mg^{2+} ions have preferentially occupied the octahedral site yielding inverse spinel ferrite [41].

The intensity of (440) plane is greater than that of (220) plane indicating presence of the highest percentage of reacting cations at octahedral site. However, incorporation of Mg ions in the spinel lattice brought about a decrease in the intestines of the previous planes depending upon the smaller ionic radius of Mg^{2+} ions [42]. But the extent of decrease in the intensity of (440) plane is greater than that of

(220) plane, where the percentage values of this decrease, respectively. This finding confirms that the Mg ferrite has a partially inverse spinel structure with formation of solid solution having magnesia–rich composition [42].

XRD pattern of Ca-Fer is shown in Figure 3.3.2; the crystal structure was identified as orthorhombic space group *Pbnm.* The unit cell parameters correspond well to literature data with diffraction peaks at 18.29°, 30.08°, 35.44°, 37.06°, 43.06°, 53.45°, 56.98° and 62.59° are indexed as the reflection planes of (111), (220), (311), (222), (400), (422), (511) and (440), respectively [43]. In additional, diffraction peaks at 24.14°,33.15° ,35.16°, 40.86°, 63.99° are indexed as the reflection (012), (104), (110), (113), (300)hematite phase



(JCPDS:01-089-2810) [44].

Figure 3.3.2: The XRD diffraction pattern of the synthesized Calcium Ferrite (Ca-Fer)

The XRD diffraction pattern of Strontium ferrite is depicted in Figure 3.3.3. The diffraction pattern indicates the formation of ferrite phase along with the presence of secondary phases such as α Fe_2O_3 and $SrFe_2O_4$ [44, 45]. Interestingly,presence of α-Fe_2O_3 phase means the system need longer and high calcination temperature for the completion of reaction. This is because, the crystal structure of α-Fe2O3 is orthorhombic hexahedron and difficult to convert into ferrite phase as compared to γ-Fe2O3 [46].

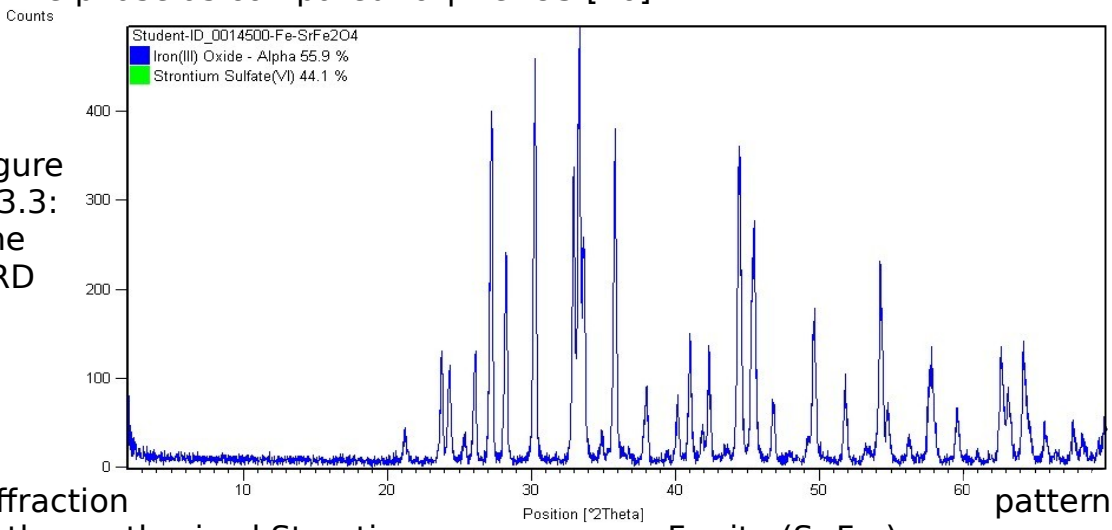


Figure 3.3.3: The XRD diffraction pattern of the synthesized Strontium Ferrite (Sr-Fer)

The existence of sharp, intense and narrower diffraction peaks indicates the formation of Sr ferrites material. The disappearance of secondary phase, however, indicates the formation of single phase M-type hexaferrite with high crystallinity. All the apparent peaks (110), (114), (107), (203), (205), (206), (208), and (303) in the diffraction pattern are similar to standard (JCPDS: 80-1198) diffraction pattern of hexagonal ferrite [46, 47].

The XRD pattern of synthesized $BaFe_2O_4$ powder is shown in Figure 3.3.4 the crystal structure was identified as orthorhombic space group *pnma,*The unit cell parameters correspond well to the literature data with diffraction peaks at32.8, 35.6, 40.5, 49.3, 54.0, 62.4 and 63.7ºare indexed as the reflection planeof(104),(110),(113),(024),(116), (214)and(300),respectively, corresponding to the rhombohedral phase of hematite (α-Fe_2O_3) [48]. The existence of sharp, intense and narrower diffraction peak at (002) indicates the formation of $BaFe_2O_4$ ferrites material [49].

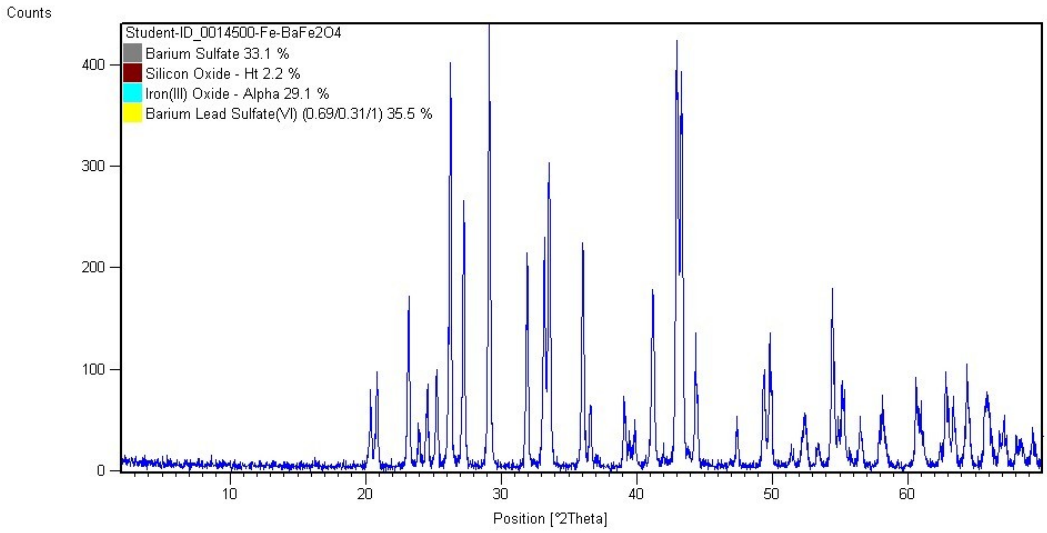


Figure 3.3.4: The XRD diffraction pattern of the synthesized Barium Ferrite (Ba-Fer)

3.4 Atomic absorption spectroscopic (AAS) analysis

Table 4.9 shows the AAS analysisresults of all ferrite samples. For Sr-Fer sample the experimental percentages of Sr^{2+}, Fe^{3+} and O^{2-}

(weight difference) were found to be 32.52 %, 41.78 %, and 25.70 %, respectively. Hence by calculating the number of moles for any element, the empirical formula $SrFe_2O_{4.3}$ is obtained, which is quite close to the theoretical formula $SrFe_2O_4$ for spinel ferrite. For Ca-Fer sample the experimental percentages of Ca^{2+}, Fe^{3+} and O^{2-} (weight difference) were found to be 17.31%,50.18 %, and 32.51 %, respectively. Hence by calculating the number of moles for any element, the empirical formula $CaFe_{2.1}O_{4.1}$is obtained, which is quite close to the theoretical formula $CaFe_2O_5$ for spinel ferrite.

Table 3.4.1: Atomic absorption spectrometric analysis of ferrite samples

samples	Element %					Empirical formula
	Ba	Ca	Fe	Mg	Sr	
Sr-Ferr	-	-	41.78	-	32.52	$SrFe_2O_{4.3}$
Ca-Ferr	-	17.31	50.18	-	-	$CaFe_{2.1}O_{4.1}$
Ba-Ferr	43.87	-	35.68	-	-	$BaFe_2O_{4.4}$
Mg-Ferr	-	-	55.84	12.15	-	$Mg\ Fe_{2.2}O_{3.7}$

For Ba-Fer sample the experimental percentages of Ba^{2+}, Fe^{3+} and O^{2-} (weight difference) were found to be43.87 %, 35.68 % , and 22.14 %, respectively. Hence by calculating the number of moles for any element, the empirical formula $BaFe_2O_{4.4}$ is obtained, which is quite

close to the theoretical formula $BaFe_2O_4$ for spinel ferrite.For Mg-Fer sample the experimental percentages of Mg^{2+}, Fe^{3+} and O^{2-} (weight difference) were found to be 12.15 %,55.84 %, and 23.92 %, respectively. Hence by calculating the number of moles for any element, the empirical formula is obtained,Mg $Fe_{2.2}O_{3.7}$ which is quite close to the theoretical formula $MgFe_2O_4$ for spinel ferrite.

Chapter Four

Conclusions

Ferrite of Mg(II), Ca (II), Sr (II), Ba (II), and Fe (II) were synthesized under normal conditions by adopting a co-precipitation method using simple salts of thesedivalent metal ions. The synthesized ferrite materials were labeled asMagnesium Ferrite (Mg-Fer), calcium Ferrite (Ca-Fer), Strontium Ferrite (Sr-Fer) and BariumFerrite (Ba-Fer) andIron ferrite(Fe-Fer), respectively. These ferrites were found to exhibit some variations in their appearances whereas their percentages yields were observed to be close. The produced ferrites were characterized with many spectroscopic techniques. The FT-IR results of the samples showed the existence of both Fe-O and M-O bands; whereas XRD diffraction data emphasized the presence of diffraction lines of the spinel type MFe_2O_4 (M=Mg, Ca, Ba, Sr or Fe) ferrites. The empirical formulas of these ferrites were calculated from

the AAS elemental analytical results, and were observed to be consistent to the theoretical formula. Only minor variations in the percentage were observed for some ferrite samples which don't affect to formula of typical spinel ferrites.

References

[1] Snoek, J.L., (1947). New Developments in Ferromagnetic Materials, Elsevier Publishing Co. Inc., New York and Amsterdam, vol 2, pp 171-176.

[2] Neel, J.L., (1951). Anti-ferromagnetismandferromagnetismproceedingsofthe physical Society London, vol 65, pp 869–885.

[3] Anderson, P. L., (1950). Anti-ferromagnetism Theory of Super exchanges interaction,*Physical Review*, vol 79, pp 350.

[4] Van-Vleck, J.H., (1950). On the theory offerromagnetic resonance, *Physical Review*, vol 78, pp 266.

[5] Yafet, Y., Kittel, C., (1952). Anti-ferromagnetic and arrangements in Ferrites, *Physical Review*, vol 87, pp 290.

[6] Cullity, B.D., Graham, C.D., (2009). Introduction to magnetic materials, published by John Wiley & Sons, Inc., Hoboken, New Jersey.vol 6, pp 175-193.

[7] Snelling, E.C., (1969). Soft ferrites properties and applications, 1st Edition, ILIFFEBooks Ltdof London. Part 2 pp 2-5.

[8] Sugimoto,M.,(1999). The past, present, and future of ferrites, *Journal of the American, society*, vol82, part 2 pp269 - 280.

[9] Moulson, A.J., (1990). Electro-ceramics materials, properties, applications,1stEdition. Chapman and Hall, London.

[10] Stuijts, A.L., Rathenau, G.W., Weber, G.H., (1954). Introduction to magmatic material *Philips Technical Review*, vol 16,pp141.

[11] Fang, H.C., Ong, C.K., (1999). Magnetic relaxation in Zn-Sn-doped barium ferrite,*Journal of Applied Physics*, vol 86, Issue4, pp 2191–2195.

[12] Harris, V.G., (2006). Ba-hexaferrite films for next generation microwave devices (invited), *Journal of Applied Physics*, vol 99, part 3, pp 8.

[13] Licht, S.,Wang. B., andGhosh, S., (1999).Synthesis and analysis of Ag2FeO4 Fe(VI) ferrate super-iron cathodes, Energetic Iron (VI) chemistry, the super-iron battery. vol 285, pp1039-1042.

[14] Sankaranarayanan, V. K., Prakash. O., Pant. R.P., and Islam. M., (2002).Lithium ferrite Nano-particle for ferro-fluid application, *Journal of Magnetism and Magnetic Materials*, vol 252, pp7-9.

[15] Morrish, H.A., Clark, P.E., (1975). High-field Mossbauer study of manganese–zinc ferrites, *Physical Review*, part2, pp280 –286.

[16] Patil, K.C., Sundar. Manoharan, S., Gajapathi,D., (1989).Preparation of high density ferrites, Handbook of Ceramicsand Composites, vol 1, pp469 - 493.

[17] Koops, C. G., (1951). On the dispersion of resistivity and dielectric constant of somefrequencies, *Physical Review*, vol 83, pp121.

[18] Auzans, E.,Zins,D.,Blums, E.,andMassart, R.,(1999). Synthesis and properties of Mn-Zn ferrite ferrofluids, *Journal of Materials Science*,vol 34, Issue 6, pp 1253-1260.

[19] Thakur, A., Singh, M., (2003). Preparation and characterization of $Mn_{0.4}Zn_{0.6}Fe_2O_4$ ferrite by citrate precursor method, *Ceramic International,* vol 29, pp 505–511.

[20]Kittel, C., (1948).On the theory of ferromagnetic resonance absorption, *Physical Review*, vol 73, pp 155.

[21] Tang, Z.X., Sorensen, C.M., Klabunde, K.J., And Hadjipanayis, G.C., (1991).Size-dependent magnetic properties o manganese ferrite fine particles, *Journal of Applied Physics*, vol 69, Issue 8, pp5279-5281.

[22] Rezlescu, N*.,* and Rezlescu, E., (1974). Dielectric properties of copper containing ferrites, *Physical status of solids*, vol 23, issue 2, pp 575-582.

[23] Smit, J.,Wijn,H.P.J., (1959). Ferrites physical properties of ferromagnetic oxides in relation to their technical applications philips technical Library, Eindhoven.1st Edition, pp155-156.

[24] Ming, Xian.,Liu,Yu. Shao., (2007). Progress in Nuclear Magnetic Resonance Spectroscopy, *Journal of magnetism and magnetic materials*, vol 308, issue 1, pp 1-170.

[25]Louh,R.,ReynoldsIII,T.G.,Buchanan*,* R.C.,(2004).Ferrite ceramic inmaterialsofelectronicsedited byBuchanan*,* R. C.,Marcel Dekker Inc.,New York,3rdEdition*.*

[26] Li, F., Evans. G., (2004).Nano porous structure prepared by an electro-chemical deposition process, *advanced materials*, vol 16, pp1597.

[27] Leu, J., (2003). Preparation and mono dispersed Fe-Mo as the catalyst for CVD synthesis for carbon nanotubes, *Chemistry of materials*, vol4,pp 242.

[28] Ravindranathan, P., Patil. K.C., (2005).Effect of firing temperature on microstructure and magnetic properties of nano-crystalline $NiZnFe_2O_4$ prepared by wet and dry method.*Journal of analytical and applied hydrolysis* ,vol 66, pp688-692.

[29] Sunder, S. Manoharan ., (1989). Electron paramagnetic resonance investigation of the Cu^{2+} ion in a variety of host lattice, *physicalProcedia ,* ICF-5 India 43-47.

[30] Yafet, Y., Kittel, C., (1952). Antiferromagnetic arrangements in ferrites, *Physical Review*, vol 87, pp 290.

[31] Jolly, L.W., (1991). The synthesis and characterization of inorganic compound, Waveland press lnc,USA, pp 524-525.

[32] Pradeep, A., Chandrasekaran,G., (2006).FTIR Study of Ni, Cu and Zn Substituted Nano-Particles of $MgFe_2O_4$,*MaterialsLetters* 60,pp371 – 374.

[33] Hafner, S., (1961). The absorption of some metal oxides with spinel structure, Zeitschrift Fur Crystallography, vol 115, pp 331–358.

[34] Waldron, R.D., (1955). Infrared spectra of ferrites, *Physical Review*, vol 99, pp1727–1735.

[35] Porta, P.,Stone,F.S., Turner, R.G.,(2013). Synthesis and Characterization of Magnesium ferrite nanoparticles by Co-precipitation method, *Journal of SolidState Chemistry,* vol11,issue 2, pp135–147.

[36] Pereira, F.M.M., Junior,C.A.R., Santos,M.R.P., Sohn,R.S.T.M., Freire,F.N.A.,Sasaki, J.M., de Paiva, J.A.C., andSombra, A.S.B., (2008). Structural and dielectric spectroscopy studies of the M-type barium strontium hexaferrite alloys ($Ba_xSr_1xFe_{12}O_{19}$). *Journalmaterial.*vol19, pp627 - 638.

[37] Hoque, S., Hakim, M., Mamun, A., Akhter, S., Hasan, M., Paul. D., Chattopadhayay, K., (2011). Study of the Bulk Magnetic and electrical properties of $MgFe_2O_4$ synthesized by chemical method, Materials *sciences and applications*, vol 2, issue11, pp 1564-1571.

[38] Ming. Ma., Yu. Zhang., Wei, Yu., Hao-ying, Shen., Hai-qian,. Zhang, Ning.Gu., (2003). Preparation and characterization of magnetite nanoparticles coated by amino silane, *Journal of Colloidsand surfacesA-physicochemical* and *engineering aspects,*vol212, pp 219-226.

[39] Cullity,B.,Stock, S.R., (2001). Elements of X-ray diffraction , 3rd Ed., publishedby Addison Wesley, U.S.A., pp 167-171.

[40] Deraz, N.M., (2013). Effects of magnesia content on spinel magnesium ferrite formation, *Journal of Electrochemical science, Applied Physics*, vol 7, pp4596.

[41] Kinemuchi, Y., Ishizaka, K., Suematsu, H., Jiang,W., Yatsui, K., (2002). Magnetic properties of nanosize $NiFe_2O_4$ particles synthesized by pulsed wire discharge, thin solid films,vol 407, issue 1-2, pp. 109–113, View at Publisher , View at Google Scholar.

[42] Deraz, N.M., Alarifi.,(2012). Novel preparation and properties of m-agnesium ferrite nano-particles,*Journal ofAnalytical*and*Applied Pyrolysis,* vol 97,pp*55*–61.

[43] Balavijayalakshmia, J., (2013). Effect of concentration on dielectric properties of
Co- Cu Ferrite- nano particles, *Physics Procedia*,vol 49, pp 49 – 57.

[44] Yuan, C.L., Hong,Y.S., Lin,C.H., (2011).Preparation, magnetic and electromagnetic properties of polyaniline/strontium ferrite/multiwalled carbon nanotubes composite*Journal of Magnetism and* Magnetic, vol323,pp1851-1854.

[45] Mali,A., And Ataie, A., (2005). Crystallization kinetics of strontium hexaferrite: correlation to structural, morphological, dielectric and magnetic properties,*Materials science,* vol53, pp1065.

[46] Qiu, J., Liang,L., Go, *M.*, (2005). Nano-crystalline structure and magnetic properties of barium ferrites, *Materialsscience and engineering,* vol393,pp361-365.

[47] Blake, R.L., Hessevick, R.E., Zoltai, T., Finger, L.W.,(1966). Tetragonalpowder diffraction,*American mineralogist,* vol51,pp123-129.

[48] Zlatkova, B.S., Nikolicb, M.V., Aleksicb, O., Dan-ningerc, H., And Halwax, E., (2009). A study of magneto-crystalline alignment in sintered barium hexaferrite fabricated by powder injection molding, *Journal of magnetism and magnetic materials*, vol321, No. 4, pp 330-335.

[49] Shang, H., Wang, J., And Liu,Q.F., (2007). Synthesis and characterization of Nano-crystalline $BaFe_{12}O_{19}$ obtained by using glucose as a fuel, *Materials science and engineering*,vol 456, issue15, pp130-132.