1.1 A brief history of magnetism

Magnetism is a venerable subject, which underwent four revolutionary changes in the course of the twentieth century – understanding of the physics, extension to high frequencies, the avalanche of consumer applications and, most recently, the emergence of spin electronics. Magnetics, in partnership with semiconductors, has evolved the technology that has created the information revolution. The history of magnetism is coeval with the history of science. The magnet’s ability to attract ferrous objects by remote control, acting at a distance, has captivated countless curious spirits over two millennia. In the middle ages, superstitions and fantasy had accreted to the “attractive force” and much egregious fantasy was debunked by William Gilbert in his 1600 monograph *De Magnete*, which was arguably the first modern scientific text [1]. The electromagnetic revolution was launched in 1820 by Hans-Christian Oersted (Denmark) and Andre-Marie Ampere and Dominique-Francois Arago (Paris). Michael Faraday’s discovery of “Electromagnetic induction” in 1821 through his intuition that the electric and magnetic forces could be conceived in terms of all pervading fields changed the world for ever.

Despite the dazzling technical and intellectual triumphs of the electromagnetic revolution, the problem of explaining how a solid could possibly be ferromagnetic was unsolved. The magnetization of iron $1.76 \times 10^6$ A/m implies extremely high surface current density as per classical physics which was implausible, but a satisfactory explanation emerged after the advent of quantum mechanics. The quantized spin angular momentum, source of electron’s intrinsic magnetic moment, known as Bohr magneton, $\mu_B = 9.274 \times 10^{-24}$ A m$^2$, explained that the magnetic properties of solids arise essentially from the magnetic moments of their atomic electrons.

The interactions responsible for ferromagnetism represented by the Weiss molecular field were shown by Werner Heisenberg in 1929 to be electrostatic in nature, originating from the quantum mechanics of the Pauli principle. Heisenberg formulated a Hamiltonian to represent the interaction of two neighbouring atoms whose total electronic spins, in units of Planck’s constant $= 1.055 \times 10^{-34}$ J s, are $S_i$ and $S_j$, namely,

$$H = -2J S_i \cdot S_j$$
Where, \( J \) is the exchange constant; \( J/k_B \) is typically in the range 1–100 K. Here, \( k_B \) is Boltzmann’s constant, \( 1.3807 \times 10^{-23} \) \( J \) \( K^{-1} \). Atomic magnetic moments are associated with the electronic spins. The quantum revolution underpinning modern atomic and solid state physics and chemistry was essentially complete in 1930. If the exchange interaction \( J \) is negative (antiferromagnetic) rather than positive, there is a tendency of spins to align antiparallel rather than parallel (negative exchange interaction). Louis N’eel pointed out in that negative exchange interaction leads to antiferromagnetism or ferrimagnetism, depending on the topology of the crystal lattice [2].

The subject of magnetism is more of an experimental one than others in the area of physics in the sense that our experimental knowledge far exceeds the theoretical understanding of the fundamental science. History of magnetism has taught us that fundamental understanding of science is not a prerequisite for technological progress. Much progress in this field is made empirically, with no recourse to basic theories. Yet fundamental understanding helps. However, quantum mechanics came into picture when researchers attempted to understand the interaction of electromagnetic radiation (microwaves or optical ranges) with magnetic materials. This led to the discovery of magnetic resonance techniques and microwave components. Recent decades have witnessed an immense expansion of magnetic applications in the areas of permanent magnets, magnetic recording, high frequency materials that has supported the tremendous progress in computers, telecommunication equipments and medical imaging. The third millennium has seen the development of *spin electronics* where scientists are trying to learn how to manipulate spin currents.

Nano-scale magnetic particles have at least one dimension in the nano-meter range i.e. 1 nm to 100 nm. In a bulk ferromagnetic material, width of the domain wall falls in the nano-scale. This is of great concern to the people working in nanomagnetism. A general feature of nano-particles is the large proportion of surface atoms. The fraction of atoms on the surface of the nano-spherical particle is \( 3d/R \), where, \( d \) is inter-atomic spacing and \( R \) is the radius of nano-particle. For example, if \( d=0.25 \) nm then fraction of atoms on the surface of a spherical nano-particle of diameter 10 nm is 15%. For a CoFe\(_2\)O\(_4\) domain wall width is 20 nm and maximum equilibrium single domain particle size is 160 nm. Small ferrimagnetic particles appear naturally in igneous rocks, ferromagnetic and ferrimagnetic particles can be synthesized by a variety of chemical methods.

**Table 1.1 The seven ages of magnetism**

<table>
<thead>
<tr>
<th>Period</th>
<th>Dates</th>
<th>Icon</th>
<th>Drivers</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ancient period</td>
<td>~2000–1500</td>
<td>Compass</td>
<td>State, geomancers</td>
<td>Iron, lodestone</td>
</tr>
<tr>
<td>Early modern age</td>
<td>1500–1820</td>
<td>Horseshoe magnet</td>
<td>Navy</td>
<td>Iron, lodestone</td>
</tr>
<tr>
<td>Electromagnetic age</td>
<td>1820–1900</td>
<td>Electromagnet</td>
<td>Industry, infrastructure</td>
<td>Electrical steel</td>
</tr>
<tr>
<td>Age of understanding</td>
<td>1900–1935</td>
<td>Pauli matrices</td>
<td>Academic</td>
<td>Alnico</td>
</tr>
<tr>
<td>High-frequency age</td>
<td>1935–1960</td>
<td>Magnetic resonance</td>
<td>Military</td>
<td>Ferrites</td>
</tr>
<tr>
<td>Age of applications</td>
<td>1960–1995</td>
<td>Electric screwdriver</td>
<td>Consumer market</td>
<td>Sm-Co, Nd-Fe-B</td>
</tr>
<tr>
<td>Age of spin electronics</td>
<td>1995–today</td>
<td>Read head</td>
<td>Consumer market</td>
<td>Multilayers</td>
</tr>
</tbody>
</table>

Materials synthesis is the foundation of experimental magnetism because the application depends upon the nature and the form of the material. The great majority of magnetic materials are studied in the research laboratory are synthetic products of complex fabrication process. Nanoparticles are usually produced by wet chemical methods. Particle size can be controlled from a few nanometers up to many micrometers, spanning the super-paramagnetic, single-domain and multi-domain regions.

Ferrimagnetic oxides (ferrites) crystallize in any one of the following four groups: Spinel, Magnetoplumbite (Hexagonal), Garnet, Orthoferrite. Ferrimagnets are imperfect anti-ferromagnets. Ferromagnetic materials differ from ferromagnetic substances in the arrangement of the atomic spins. In ferromagnetic substances there are at least two directions in which the atomic dipoles are oriented. Magnetite (Fe\(_3\)O\(_4\)) is a standard example of spinel ferrite or ferro-spinel having a crystal structure of mineral spinel (MgAl\(_2\)O\(_4\)). The structure of spinel was elucidated by Bragg in 1915.
[3]. It has space group Fd\(\bar{3}\)m, 8 molecules \((\text{AB}_2\text{O}_4)\) per unit cell (8 A-site atoms, 16 B-site atoms and 32 oxygen ions) with X-ray density 5.195 g/cm\(^3\) with lattice constant 8.397 Å. In a closed packed cage made by 32 oxygen atoms, divalent Fe\(^{2+}\) ions occupy octahedral sites and trivalent Fe\(^{3+}\) metal ions are evenly distributed between tetrahedral and octahedral sites. The magnetic moments on A-site ions are antiparallel to the all the B-site magnetic moments with magnetization along (1 1 1) direction. The net magnetic moment at absolute zero is 4 \(\mu_B\) per formula unit with Curie temperature 860 K.

The crystal structure of a spinel ferrite can be regarded as an interlocking network of positively-charged metal ions (Fe\(^{3+}\), Me\(^{3+}\)) and negatively-charged divalent oxygen ions. The spinel structure is by far the most widely used ferrite, so much so that the term is almost synonymous with the ferrite. In a spinel MgAl\(_2\)O\(_4\), Al\(^{3+}\) is usually replaced by Fe\(^{3+}\) or other trivalent ions like Cr\(^{3+}\) or Ga\(^{3+}\) and Mg\(^{2+}\) can be replaced by divalent metal ions Mn\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Fe\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\) or more often combination of these. The presence of Mn\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Co\(^{2+}\) and Fe\(^{2+}\) can be used to provide the unpaired electron spin and therefore part of the magnetic moment of a spinel. Other divalent metal ions such as Mg\(^{2+}\) or Zn\(^{2+}\) or monovalent Li\(^{+}\) are used to disturb or disproportionate the distribution of Fe\(^{3+}\) ions among the A- and B-sites of the spinel lattice to provide or to increase the net magnetic moment [4]. With regard to the strength of interactions between site magnetic moments, the negative exchange interaction between magnetic ions on different sites depends upon the distances between these magnetic ions and the oxygen ion that links them and also on the angle between the three ions. The interaction is strongest for an angle of 180° and also where the interatomic distances are the shortest. In A - A and B - B cases, the angles are too small or the distances between the metal ions and oxygen ions are too large. The best combination of distances and angles are found in the A - B interactions. Therefore, the interaction between moments on the A and B - sites is the strongest. The B - B interaction is much weaker and the most unfavorable situation occurs in the A - A interaction. The magnetic properties of spinel ferrites are governed by relative strengths of inter (A - B) sublattice and intra (B - B, A - A) sublattice interactions. When A - B interaction is the strongest the ferrite has collinear type of magnetic ordering in which the A- and B - sites magnetic moments are antiparallel. Thus, the strongest A - B interaction renders undiluted spinel ferrimagnetic. Upon magnetic dilution by substitution of diamagnetic divalent metal cations, inter and intra sublattice magnetic interactions become comparable leading to collapse of collinear magnetic ordering and effective magnetic moments are created within the ferromagnetic structure by local canting around the magnetic imperfection [5].

After taking the bird eye view of the development of magnetism and spinel ferrites, let us turn to the background to the research work carried out in the thesis. It is well known that the method of preparation greatly influences the structural and magnetic properties of ferrites. This means that the synthesis parameters play an important role with regard to the properties of the final ferrite products. The ferrites can be prepared by different methods. The problem of synthesis of ferrites is to prepare the ferrite materials keeping in mind the requirement of physical properties of the final products. A goal common to all the ferrites is the formation of the spinel structure. The old conventional method for ferrite preparation is ceramic technique. The starting materials are conventionally oxides or precursors of oxides of the final products. Non-mixture is prepared by different methods. The problem of synthesis of ferrites is to use the final products.

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at 1100°C. In general, calcinations temperature is about 300°C lower than the final sintering temperature. Today, the large majority of commercial ferrite powders are prepared by the ceramic process. Most non-conventional process involves producing the ferrite powders by wet-chemical methods involving co-precipitation, hydrothermal synthesis, sol-gel synthesis etc. The need for power materials for increasingly higher frequencies would be satisfied by fine-grained ferrites. The fine-grained ferrites materials can be prepared by either top-down or bottom-up method. In a top-down method, ceramically synthesized ferrite powders milled by using high energy ball mill for long time duration or they can also be prepared by prolonged high energy ball milling of oxide ingredients. In bottom-up methods, ferrite particles are grown through nucleation/condensation/agglomeration by using various wet-chemical routes. In the present thesis work, the selected mixed ferrite nano-particles are synthesized by six different wet-chemical methods.

1.2 Literature survey

In the ceramic sintering process, iron oxide (α-Fe$_2$O$_3$) used has rhombohedral crystal structure which should be changed to cubic to accommodate metal ions in the sites. This requires high processing temperature. On the contrary, in the co-precipitation method, γ-Fe$_2$O$_3$ is expected to form which is a defect spinel that can easily accommodate metal ions in the sites and therefore requires lower synthesis temperature [7]. The fine particle nature is lost by high temperature sintering to get the final ferrite product. The co-precipitation method which gives very fine particles with homogeneity at atomic level is always preferred. The main advantages of co-precipitation method are: greater homogeneity, greater reactivity, high purity and no grinding; very fine nano-meter size particles and elimination of high temperature sintering. Numerous research reports are available on ferrites synthesized by co-precipitation methods [8 - 13]. Akashi [14] reported achieving extremely good magnetic properties in commercial ferrites through co-precipitation synthesis. Goldman obtained Mn-Zn ferrite materials with los factor of the order of 1 x 10$^{-6}$ by using co-precipitation method [15]. Yu also reported forming mono disperse (individual unagglomerated) particles of Mn-Zn ferrites [16]. Goldman and Knese prepared Ni-Zn ferrites by co-precipitation method by using organic analogous to ammonia (diethylamine) [15, 17]. Aluminium doped γ-Fe$_2$O$_3$ was synthesized by Filho by co-precipitation method [18]. Bo and Zeyi reported preparation of Mn-Zn ferrites by oxalates co-precipitation and oxidation process. The disadvantage of the use of oxalates is high cost [19]. The materials like Lithium ferrite is difficult to prepare by co-precipitation as there are few insoluble lithium salts. Date used ultrafine particles of strontium ferrites by co-precipitation method [20]. Very fine particle Ni-ferrite prepared by co-precipitation method [21] showed non-collinear spin structure. Sato reported Co-Zn ferrites and Zn-ferrite prepared by co-precipitation technique having high magnetization with particle size within 8-12 nm [22]. Ultrafine particles of CdFe$_2$O$_4$ were produced by Yokoyama using co-precipitation with NaOH [23]. They found much higher saturation magnetization compared to its bulk ceramic counterpart. Iwauchi [24] prepared very fine magnetite particles by using precipitation of ferrous sulfate and oxidation of ferrous hydroxide in air at 70°C for magnetic tonner application. It is important to note that in the co-precipitation method the solubility product constant of all the hydroxides involved is always exceeded, if starting solution containing chlorides or sulfates in stoichiometric proportion is added to the precipitant (NaOH or NH$_4$OH) [25]. This prevents the sequential precipitation and simultaneous precipitation of the hydroxides is achieved. There are reports on studies on magnetic and electrical properties Ni-Cd [26, 27], Mg-Mn [28], Zn-Co-Fe-Al-O spinel [29] ferrites prepared by co-precipitation method.

There are various methods of preparation of nano-structured powders [30]. They are: co-precipitation, sol-gel, flash combustion, hydrothermal synthesis, auto-Combustion, polymeric precursor, citrate precursor method etc.

The sol-gel technique is new in which small colloidal particles are first formed in solution usually by hydrolysis of organic compounds. Ni-ferrite nano-particles were prepared by sol-gel method using polyacrylic acid as chelating agent of 5 - 30 nm size [31]. Nano crystalline Ni-Cu-Zn ferrites were prepared by sol-gel auto combustion technique [32]. The preparation of spinel ferrites by sol-gel, auto-combustion technique is given in detail in a review article by Andris Sukta [33]. Nano structured Ni-Zn ferrites were synthesized for microwave applications by sol-gel technique [34, 35]. Ultra-fine Co-ferrite particles were also prepared by sol-gel method [36].

Among the available solution-chemistry routes, combustion technique is capable of producing nano crystalline powders of oxide ceramics, at lower
calcinations temperature in a surprisingly short time [37 - 43]. It is important to note that in the co-precipitation or hydrothermal method washing and drying process sometimes causes loss of metal ions which reduces their suitability for large scale production of ferrites. There are excellent review articles covering all aspects of combustion synthesis with classification of reactions as per materials with thermodynamics and reaction kinetics [44 - 47]. Mn-Zn, Li-Zn ferrites were prepared by combustion method [48, 49]. The combustion synthesis based on exothermicity of redox reaction between metal nitrates (oxidants) and tetraformal trisazine or oxalic acod dihydrazide (fuels) for spinel ferrites, garnets and orthoferrites is explained [50, 51]. The flash combustion synthesis of ABO₃ and AB₂O₄ type compounds is discissed by Augustin [52]. The nano-particles of CuFe₂O₄ and Mn-Zn ferrites have been prepared by flash combustion technique using acetates [53, 54].

There are scholarly reports on the preparation of nano structured ferrites by citrate precursor method [55 - 67]. The citrate precursor method is inexpensive to obtain nano-sized, homogeneous and highly reactive ferrite powders. It offers possibility of introducing small amount of trivalent or divalent substitution.

Hydrothermal synthesis involves the aqueous reaction of constituents under high temperature and vapour pressure in a sealed reaction vessel. Somiya and Roy have given a detailed note on hydrothermal synthesis of oxide fine powders [68]. Hasegava used hydrothermal synthesis to control the particle size of Fe₂O₃ particles and Mn-Zn ferrites [69]. Verma synthesized MgFe₂O₄ nano-particles by microwave assisted hydrothermal method [70]. Rath prepared nano-particles of Mn-Zn ferrites by hydrothermal reaction and observed that particle size is strongly influenced by Zn-content [71].

Polymeric precursor method (PPM) involves the rapid evaporation of poly vinyl alcohol added to a mixed metal nitrate solution, followed by pyrolysis of the dried mass [72]. The polymeric precursor method (PPM) [73, 74] is associated with the formation of a metallic complex using a polymer, such as PVA, PVP etc. Polymerization is promoted by heating the complex in the presence of a polymer such as PVA [75]. A homogeneous resin, the polymeric precursor is produced, in which the metal ions are uniformly distributed within the organic matrix [76]. The fine particle powders of Co ferrites were prepared by PPM [77]. Nano-crystalline Co-ferrite was synthesized by PPM and the effect of calculation temperature on its properties was studied [78].

1.3 Aim of the present work

It is known that Cobalt ferrite is a partially inverse spinel having degree of inversion sensitive to method of preparation of the specimen. Moreover, Co³⁺ ions introduces a uniaxial anisotropy in the material due to more spin-orbit coupling than the other 3d transition metal ions and its effect has been found to be more pronounced when it occupies the octahedral sites. The strong binding of the magnetization vector to the crystal axis produces low permeabilities and high coercive force. MnFe₂O₄ is almost normal ferrite with 20% inversion and net magnetic moment of 4.6μ₅₀ per molecule and coarse grained Mn-ferrite does not exhibit coercivity. The deviation from the Neel’s moment impies of collinear spin structure is a controversy. NiFe₂O₄ is an inverse ferrite as the Ni²⁺ ions have marked octahedral site preference hence collinear ferrimagnet and soft ferrite. Co-Ni mixed ferrites find applications as magnetostrictive ferrites, magneto-mechanical sensors, bio-magnetic applications [79]. Ultrafine Co-Mn ferrite particles were prepared by sol-gel method and their magnetic properties were studied [80]. There is a report on magnetostrictive properties of Co-Ni ferrites nano-particles [81].

In view of the literature survey on various synthesis methods of nano structured ferrites it was resolved to synthesize Co-Mn and Co-Ni ferrites by six different synthesis methods: Auto Combustion Method (ACM), Co-precipitation Method (CPM), Citrate Precursor Method (CPM), Flash Combustion Method (FCM), Hydrothermal Method (HTM) and Polymeric Precursor Method (PPM) with the compositions

\[
\text{Co₃Mn}_{1-x}\text{Fe}_{x}\text{O}_4 \quad \text{(x = 0.0 to 1.0, in step: x = 0.2)}
\]

\[
\text{Co}_{x}\text{Ni}_{3-x}\text{Fe}_x\text{O}_4 \quad \text{(x = 0.0 to 1.0, in step: x = 0.2)}
\]

Main aim was to standardize each synthesis technique mentioned above so that nano-ferrite powder in a large quantity can be produced. All the nano-structured ferrite powders were characterized by powder X-ray diffraction, EDAX, SEM, TEM, FTIR, Raman spectroscopy and magnetic measurements.
Chapter - 1

INTRODUCTION AND LITERATURE REVIEW

References:
9. R. G. Kulkarni, H. H. Joshi, Comparison of magnetic properties of MgFe2O4 prepared by wet-chemical and ceramic methods, J. Solid State Chemistry, 64(2), (1986) 141-147
INTRODUCTION AND LITERATURE REVIEW

43. Y. Liu, Y. Zhang, J. D. Feng, C. F. Li, J. Shi, R. Xiong, Dependence of magnetic properties on crystallite size of CoFe2O4 nanoparticles synthesised by auto-combustion method, J. Exp. Nanosci, 4(2), (2009) 159-168

54. R. V. Mangalaraja, S. Ananthakumar, P. Manohar, M. Avano, Characterization of Mn0.5Zn0.5Fe2O4 synthesized by flash combustion technique, Materials Sci. Eng. A, 367(1), (2004) 301-305
56. A. H. Wahba, M. B. Mohamed, Structural, magnetic, and dielectric properties of nanocrystalline Cr-substituted Co0.8Ni0.2Fe2O4 ferrite, Ceramic Int., 40(4), (2014) 6127-36
Chapter - 1  

67 C. Vinuthna, D. Ravinder, R. M. Raju, Characterization of Co\textsubscript{1-X}Zn\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4}, Nano Spinal Ferrites Prepared By Citrate Precursor Method, Int. J. Eng. Res. Appl., 3(6), (2013) 645-660


69 F. Hasegawa, K. Watanabe, K. Nakatsuka, Size control of Mn-Zn ferrite particles synthesized by the hydrothermal, Ferrites Proc. ICF6, Tokyo, Japan, 112(1992)

70 S. Verma, P.A. Joy, Y. B. Kholiam, H. S. Potdar, S. B. Deshpande, Synthesis of nanosized MgFe\textsubscript{2}O\textsubscript{4} powders by microwave hydrothermal method, Mater. Lett., 58(6), (2004) 1092-95


72 T. Tsujii, M. Nagao, Y. Yamamura, N. T. Tai, Structural and thermal properties of LiMn\textsubscript{2}O\textsubscript{4} substituted for manganese by iron, Solid State Ionics, 154, (2002) 381-386

73 S. Yamamoto, M. Kakihama, S. Kato, A polymer complex solution route to the low-temperature synthesis of tetragonal Zr_{0.65}Co_{0.35}O\textsubscript{2} with a reduced amount of organic substance, J. Alloys & Compounds, 297 (2000) 81-86


