

*Advances in
Nanoscience and Nanotechnology*

Nanomaterials

Synthesis, Characterization
and Applications

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Sabu Thomas, PhD
Mathew Sebastian, MD
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NANOMATERIALS

Synthesis, Characterization, and Applications

Advances in Nanoscience and Nanotechnology

Volume 3

NANOMATERIALS

Synthesis, Characterization, and Applications

Edited by

**A. K. Haghi, PhD, Ajesh K. Zachariah, and
Nandakumar Kalarikkal, PhD**



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Advances in Nanoscience and Nanotechnology

Series Editors-in-Chief

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List of Abbreviations

ADC	Azodicarbonamide
AgNO ₃	Silver nitrate
CdS	Cadmium sulfide
CH ₃ OH	Methyl alcohol
CoFe ₂ O ₄	Cobalt ferrite
CT	Charge transfer
DDI	Dipole-Dipole interactions
DLS	Dynamic light scattering
DMIM	Discontinuous metal-insulator magnetic multilayers
Ea	Activation energy
EDS	Energy dispersive X-ray spectroscopy
EMI	Electromagnetic interference
EPD	Electrophoretic deposition
ESD	Electrostatic discharge
Fe ₂ O ₃	Hematite
FMR	Ferromagnetic resonance
FT	Fourier transform
GDVDP	Glow discharge vapor deposition polymerization
GMM	Mie-Maxwell-Garnett
GMR	Giant magnetoresistance
HA	Hydroxyapatite
Hc	Magnetic coercivity
HRTEM	High-resolution TEM
MA	Mechanical alloying
MB	Methylene blue
MMG	Mie-Maxwell-Garnett
MNCF	Metal nanocluster composite film
MR	Magnetoresistive
Ms	Magnetization
NCs	Nanoclusters
NiCCF	Nickel-coated carbon woven fabric
NiNS	Nickel nanostrands
NPs	Nanoparticles
PMDA-ODA	Dianhydride-4,4 oxydianiline
PPMS	Property measurement system
PVA	Poly(vinyl alcohol)
ROS	Reactive oxygen species
RTM	Resin transfer mold
SAED	Selected area electron diffraction
SEF	Surface enhanced fluorescence
SEM	Scanning electron microscopy

SERS	Surface enhanced raman spectroscopy
SiO ₂	Silica
SnO ₂	Tin oxide
SPM	Superparamagnetic
SPR	Surface plasmon resonance
Tanδ	Power loss
TEM	Transmission electron microscope
TiO ₂	Titania
TOF	Time-of-flight
UTS	Ultimate tensile strength
UV	Ultraviolet
VSM	Vibrating sample magnetometer
XRD	X-ray diffraction
ZnO	Zinc oxide
ZnS	Zinc sulphide
Er	Dielectric constant
Σdcb	Conductivity

Preface

The history of the nanomaterial begins from old days of alchemists. The science of “nano” started in 1959, after Richard Feynman’s famous talk at the annual meeting of the American Physical Society describing the molecular machines building with atomic precision titled as “There’s Plenty of Room at the Bottom” and he predicted that a revolution in the field of science and technology was awaiting. In 1974, Norio Taniguchi, a Japanese scientist, coined the term “nanotechnology” in a paper on ion-sputtering machining. A technical paper discussing the new technology was presented after seven years from Taniguchi’s introduction of new term. It was Eric Drexler who presented the first technical paper on molecular engineering to build with atomic precision. Since then many studies were done in the field of nanotechnology.

The present book is mainly centered on the production of different types of nanomaterials and their applications. The book can be grouped as:

- synthesis of different types of nanomaterials
- characterization of different types of nanomaterials
- applications of different types of nanomaterials including the nanocomposites

The book is intended to be a reference for basic and practical knowledge about the synthesis, characterization, and applications of nanotechnology for students, engineers, and researchers. Chapter 1 deals with the synthesis of oxide nanomaterials focusing on lithium ferrites. They form a very important group of materials. They are magnetic material having varied technological applications that can be fabricated by various synthesis methods such as conventional and nonconventional methods. Ferrites were generally produced by a ceramic process involving high temperature solid-state reactions between the constituent oxides/carbonates. Shape-controlled synthesis, characterization, and optical applications of silver nanostructures are described in Chapter 2. It discusses novel methods for chemical synthesis of silver nanoparticles of different size and shapes, such as nanorod, nanospindle, nanocube, nanosphere, nanoellipsoid, and some plate-like structures.

Chapter 3 discusses the growth and characterization of metal nano-sized branched structures on insulator substrates by electron-beam-induced deposition. Using an electron-beam-induced deposition (EBID) process in a transmission electron microscope, the authors fabricated a self-standing metal nano-sized branched structures including nanowire arrays, nanodendrites, and nanofractal-like trees, as well as their composite nanostructures with controlled size and position on insulator (SiO_2 , Al_2O_3) substrates. The techniques such as high-resolution transmission electron microscopy and X-ray energy dispersive spectroscopy and the growth mechanism are discussed.

Bone tissue diseases are among the most disabling pathologies and affect an increasing number of people worldwide. The diseases that most seriously impact people’s lives and activities are those involving long bone portions subjected to mechanical load. The impact of such problems is particularly relevant among aged people (i.e. due to osteoporosis), but in the last decade the number of relatively young patients

is continuously increasing due to modern lifestyles that include intense sports activity, tendency to obesity, etc. Chapter 4 describes the smart biomaterials obtained by biomorphic transformation. Chapter 5 discusses the porous nanostructure Ti-alloys for hard tissue implant applications. Formation of Ti-6Al-4V, Ti-15Zr-4Nb and Ti-6Zr-4Nb porous nanocrystalline bioalloys is described in Chapter 5.

Chapter 6 discusses synthesis of water-dispersible carbon nanotube–fullerodendron hybrids. Chapter 7 discusses nitrogen doping on TiO_2 via the sol gel method and improvement of properties for N-doped systems when compared to the post preparation N doping processes. Chapter 8 discusses the production of densely packed films of titanium dioxide (TiO_2) nanoparticles via electrophoretic deposition (EPD). Chapter 9 discusses the magnetic dye-adsorbent catalyst synthesized via hydrothermal processing. The magnetic dye-adsorbent catalyst consists of a core-shell nanocomposite with the core of a magnetic ceramic particle (such as mixed cobalt ferrite and hematite, and pure cobalt ferrite) and the shell of nanotubes of dye-adsorbing material (such as hydrogen titanate).

Composite materials formed by metal nanoclusters embedded in dielectric films (Metal Nanocluster Composite Film, MNCF) are the object of several studies owing to their peculiar properties suitable for application in several fields, such as nonlinear optics, photoluminescence, catalysis, or magnetism. Chapter 10 describes the plasmonic aspects of synthesis of metal nanoclusters in dielectric matrices by ion implantation. Chapter 11 discusses different approaches for the development of nanocomposites. Chapter 12 describes electrically conductive nanocomposites for structural applications. Electrical properties of CrO_2 modified ZrO_2 of a cubic (c) crystal structure are discussed in Chapter 13. Chapter 14 describes poly (methyl methacrylate) nanocomposites filled with brookite nanocrystals.

— **A. K. Haghi, PhD, Ajesh K. Zachariah,
and Nandakumar Kalarikkal, PhD**

1 Synthesis of Oxide Nanomaterials

*Ibetombi Soibam, Sumitra Phanjoubam,
and Chandra Prakash*

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1.1 INTRODUCTION

The nanomaterials have unique properties for some exceptional as well as ordinary applications. In the past few years due to their scientific importance fundamentally and technologically nanoparticle systems have received much attention, In this thrust, area of research lithium ferrites form a very important group of materials. Lithium ferrites which are magnetic material having varied technological applications can be fabricated by various synthesis method such as conventional and non-conventional method. Ferrites were generally produced by ceramic process involving high temperature solid state reactions between the constituent oxides/carbonates. The properties of ceramics like morphology, particle size distributions, magnetic properties, and so on are strongly dependent on the features of the starting powder. This is in particular true for lithium based ferrites. One of the effective means to control the powder characteristics

is to modify the powder synthesis process itself. The different methods have been proposed such as sol-gel, auto-combustion, coprecipitation, sol-gel auto combustion, Pechini method, and so on. Among the synthesis methods, citrate precursor method is one which is gaining importance for preparing fine grained ferrite powders for suitable purposes. The method appears to be simple and convenient as it neither requires expensive chemicals such as alkoxides which are used in sol-gel processing nor equipment like autoclaves for combustion process. On the other hand, the final product obtained is in the nanometer range, exhibit high purity, chemical homogeneity, and compositional control. The magnetic properties are immensely enhanced. The preparation of conventional ceramic method as well as the non-conventional method like chemical coprecipitation and citrate precursor is discussed, where emphasis is given to citrate precursor synthesis method. A particular series of samples of Li-Zn-Ni ferrite is presented along with their magnetic and Mössbauer characteristics.

The importance of fabrication and the understanding of the magnetic properties of oxides of metals attracted scientist and engineers from various fields. The lithium ferrite is one of the most used versatile magnetic materials. They are important components for microwave device and memory core due to their high values of Curie temperature, saturation magnetization, and so on [1, 2]. A number of lithium ferrite compositions comprising of the oxide of lithium and iron, and if desired the oxides of other metals such as Mn, Ni, and Zn are known to be useful in applications requiring soft ferrimagnetic properties. The lithium ferrites are usually synthesized and have been prepared by mixing and milling together powder mixture of lithium carbonate, iron oxide, and oxides of other suitable metals. After prolonged milling the powder mixture is calcined at an elevated temperature of about 1,000°C to co-react the individual oxides into the spinel lithium ferrites which is then processed into the desired components [3, 4]. The solid state reaction has some inherent disadvantages like chemical inhomogeneity, introduction of impurities during ball milling, and so on. The high temperature induced lower magnetization due to formation of Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$. However, most of the factors degrading the properties are overcome in chemical synthesis method. The art of preparing lithium ferrite by conventional method is not suitable for preparing chemically uniform lithium ferrites of extremely small grain size. The quest for synthesis of small grain size demands the synthesis of ultrafine ferrite materials [5]. Consequently, it led to the discovery of various synthesis methods. Several patents disclose various wet chemical techniques namely sol-gel, auto combustion, coprecipitation, Pechini method, and so on [6-9]. In the chemical coprecipitation process an aqueous solution of suitable salts of iron, lithium, and other desired, suitable materials is mixed with a precipitating agent that will cause the precipitation of a fatty acid salt of lithium with the hydroxides of the other metals present in the solution. The precipitate represents a substantially uniform mixture of precursor compounds of the ferrite metals. The precipitate is filtered from the mother liquor and dried. The dry precipitate is heated in air at an elevated temperature, preferably about 200°C to dehydrate the precipitate and to burn out carbonaceous matter leaving a residue of the oxides of the respective metals. The particles are then heated at a temperature of 400–500°C to co-react the lithium oxide, ferric oxide, and other metal oxides present to form a spinel lithium ferrite. At this stage, the ferrite particles which are extremely

small in size about 100 Angstrom are formed. It is then sintered at about 1,100°C. The sintering operation results in some grain growth, although such growth can be advantageously inhibited by the presence of a small amount of bismuth. It is to be noted that the grain size is significantly smaller than the grain size obtained in conventionally prepared lithium ferrites. However, the coprecipitation process takes a very long duration to obtain the required materials. This is to overcome in the sol-gel auto combustion process also known as the citrate precursor method. In this method, the respective nitrates and citric acid are heated making a spontaneous combustion process to occur giving the required ferrite sample in just a few second. A brief discussion of what is spinel structure ferrite, different preparation methods, basic magnetic, and Mössbauer background and some characteristic properties of Li-Zn-Ni ferrites prepared by citrate precursor method is given.

1.2 SPINEL STRUCTURE FERRITES

The spinel structure ferrites have the general formula MFe_2O_4 , where M represents a divalent metal ion. The divalent metal ion can be one of the divalent ions of the transition elements like Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Mg^{2+} , or a combination of these ions, or a combination of ions having average valency of two, like $0.5Li^{1+} + 0.5Fe^{3+}$ as in $Li_{0.5}Fe_{2.5}O_4$. The trivalent ion such as Al^{3+} or Cr^{3+} ion and tetravalent ion such as Ti^{4+} or Ge^{4+} ion can completely or partly replace the Fe^{3+} ions in MFe_2O_4 .

The crystal chemistry of compounds crystallizing in spinel structure has been extensively dealt with by Gorter [10], Hafner [11], and Blasse [12] although it was first determined by Bragg [13] and Nishikawa [14]. The unit cell having spinel structure is shown in Figure 1.

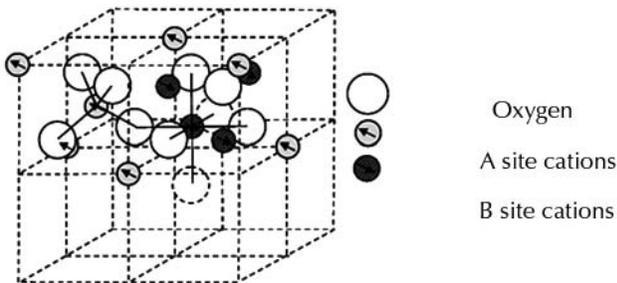


FIGURE 1 Structure of spinel ferrite.

The spinel crystal structure primarily depends on the oxygen ion lattice [10-13], the radii of the oxygen ions ($\sim 1.32\text{\AA}$) being several times larger than the radii of the metallic ions (0.6\AA and 1.0\AA). The crystal structure can consequently be thought of as being made up of the closest possible packing of oxygen ions, that is it forms an fcc

lattice leaving two kinds of interstitial sites, the tetrahedral or the A site and the octahedral or the B site. A metallic ion located at A site has four nearest oxygen ion neighbors forming a regular tetrahedron and is said to be in a site of tetrahedral coordination, whereas, a metallic ion in octahedral site has six nearest oxygen ion neighbors forming a regular octahedron and the metallic ion is in a site of octahedral coordination. The tetrahedral site has smaller volume compared to octahedral site and both types of sites are smaller in size compared to oxygen ion diameter.

In the unit cell of a spinel lattice there are eight molecules of MFe_2O_4 consisting of 32 oxygen ions forming a cubic close packed structure, 8 divalent ions and 16 trivalent ions. The 32 oxygen ions leave 64 tetrahedral interstices (A) site and 32 octahedral interstices (B) site. Of these only 8 A sites and 16 B sites are occupied by the metal ions [14, 15].

To describe the structure, the unit cell with cell edge 'a' can be subdivided into eight octants with edge $\frac{1}{2}a$. Two adjacent octants are shown in Figure 2.

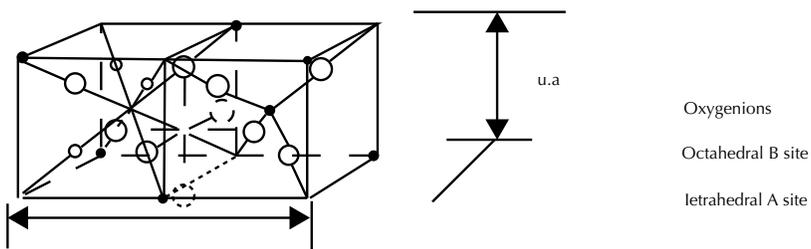


FIGURE 2 Two adjacent cubes showing two octants of the spinel structure.

The oxygen ions have identical positions in all the octants. Each octant contains four anions, which form the corners of a tetrahedron. The interstitial positions occupied in any two adjacent octants are different but are the same in two octants sharing an edge. If the ionic arrangement in any two adjacent octants are given, the unit cell can be constructed by translation of the two octants along the three (110) axes. The surrounding of a tetrahedral ion by the other ions has strictly cubic symmetry but is not the case for an individual octahedral ion. The octahedral ions, of course are cubically surrounded by the oxygen ions but not by the neighboring metal ions.

It has been mentioned earlier that oxygen ions form an fcc structure. But in the real case there is existence of slight deviations due to deformation caused by the metal ions. The tetrahedral sites are too small to accommodate a metal ion, so that when a metal cation fills a tetrahedral A site. It displaces equally the four oxygen ions outwards along the body diagonals of the cube. These four oxygen ions still occupy the corners of an enlarged tetrahedron and the symmetry around each A ion retains cubic symmetry. But the four oxygen surrounding the B site ion is shifted, in such a way, that this oxygen tetrahedron shrinks by the same amount as the first expands. Therefore, the symmetry is no longer cubic but is a trigonal symmetry such that a trigonal field appears on the B site. This field is a function of the oxygen parameter, u , which is a qualitative measure of the displacement. It is given by the distance between an oxygen

ion and a face of the cube, which is put equal to au , where ‘ a ’ is the cell edge. The ideal fcc structure has oxygen parameter $u_o = \frac{3}{8}$.

Spinel ferrites can be classified into three categories, *viz.* normal, inverse, and mixed ferrites on the basis of site occupancy by divalent and trivalent metal ions.

Normal Ferrites

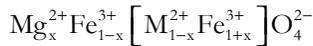
The kind of ferrites in which all the tetrahedral sites are occupied by the eight divalent cations and the octahedral sites by the 16 trivalent metal ions, are termed “normal” ferrites. Examples are zinc ferrite, $Zn^{2+}[Fe^{3+}]O_4$, cadmium ferrite $Cd^{2+}[Fe^{3+}]O_4$, and so on, where the cat ions outside the square brackets occupy A site and those within the square bracket occupy the B site.

Inverse Ferrite

In this ferrite eight out of the 16 trivalent metal ions occupy tetrahedral sites, and the octahedral sites are occupied by eight divalent metal ions and the remaining eight trivalent cations. Examples are magnetite, nickel ferrite with the respective compositional formula as $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4^{2-}$ and $Fe^{3+}[Ni^{2+}Fe^{3+}]O_4^{2-}$.

Mixed Ferrites

This kind of ferrites is neither completely normal nor completely inverse since the A and B sites are randomly occupied by both divalent and trivalent metal ions. An example of this category of ferrites is magnesium ferrite, $MgFe_2O_4$ with the general cation distribution represented as :



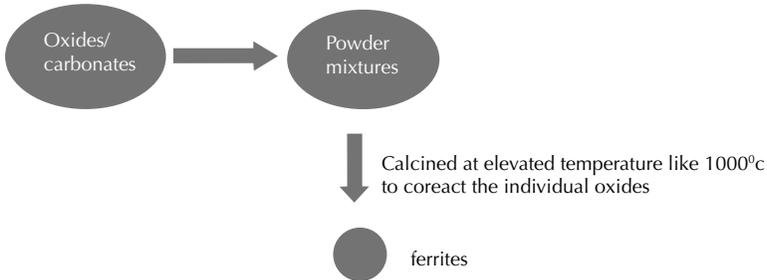
1.3 PREPARATION OF FERRITES

1.3.1 Conventional Ceramic Method

Ferrites are usually synthesized and have been prepared by mixing and milling together the powder mixture of lithium carbonate, iron oxide, and oxides of other suitable metals [16]. It is shown in Figure 3. The reactants have been weighed out in the required amount and then mixed. For small quantity of less than 20 g manual mixing may be done using agate mortar and pestle. Mostly, agate made of porcelain is used as it is hard and unlikely to contaminate the mixture. Homogenization is made by adding sufficient amount of a volatile organic liquid like acetone or alcohol which gradually volatilizes after 10–15 min of grinding and mixing. If the total quantity is much larger than 20 g manual mixing is not advisable and in such cases mechanical mixing is better using a ball mill but may take several hours. After prolonged milling the powder mixture is calcined at an elevated temperature like 1,000°C to co-react the individual oxides.

Solids do not usually react together at room temperature over normal timescales, so, it is necessary to heat them to much higher temperature often 1,000–1,500°C, in order for reaction to occur at an appreciable rate. The heating schedule to be used depends on the form and reactivity of the reactants. If one or more of the reactants is an oxysalt, the first stage of reaction must be decomposition of the oxysalt and

mixture should be heated first at an appropriate temperature for few hours such that decomposition occurs in controlled manner. If the stage is not done decomposition will occur vigorously and may cause sample to spit out of container. The reaction to give final product usually requires hours or even days depending on reaction temperature. However, this art of preparing lithium ferrite are not suitable for preparing chemically uniform lithium ferrites of extremely small grain size.



Mixing and Milling

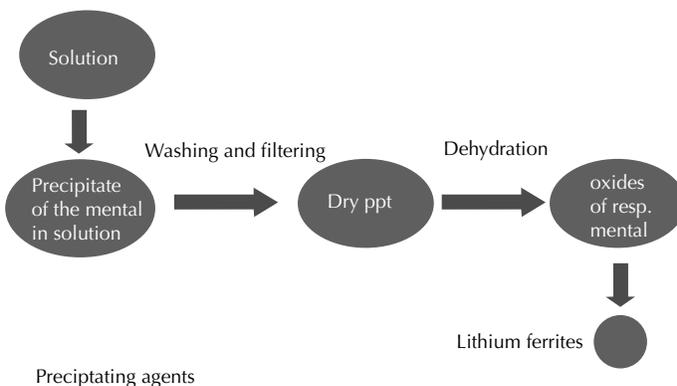
FIGURE 3 Ceramic method of preparing ferrites.

1.3.2 Non-Conventional Method

There are several non-conventional methods but here we give a basic outline of the chemical coprecipitation method and the citrate precursor method.

Chemical Coprecipitation Method

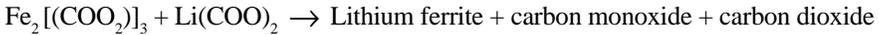
In the chemical coprecipitation (Figure 4) an aqueous solution of suitable salts of iron, lithium, manganese, and other desired, suitable materials is mixed with a precipitating agent that causes the precipitation of a fatty acid salt of lithium with the hydroxides of the other metals present in the solution. The precipitate represents a substantially uniform mixture of precursor compounds of the ferrite metals on an atomic scale. The precipitate is filtered from the mother liquor and dried.



Precipitating agents

FIGURE 4 Chemical coprecipitation method of preparing ferrites.

The dry precipitate is heated in air at an elevated temperature, preferably about 200°C to dehydrate the precipitate and to burn out carbonaceous matter leaving a residue of the oxides of the respective metals. The particles are then heated at a temperature of 400–500°C to co-react the lithium oxide, ferric oxide, and other metal oxides present to form a spinel lithium ferrite. Because of high degree of homogenization, much lower reaction temperature is sufficient for reaction to occur. The overall reaction for formation of lithium ferrite may be written as:



It is then sintered at about 1,100°C. The sintering operation results in some grain growth, although such growth can be advantageously inhibited by the presence of a small amount of calcium, so that an ultimate smaller grain size is obtained. It is to be noted that the grain size is significantly smaller than that obtained in conventionally prepared lithium ferrites [17]. The method does not work well in cases where two reactants have very different solubilities in water and the reactants do not precipitate at the same rate. However, the coprecipitation process takes a very long duration to obtain the required materials and is often not suitable for preparation of high purity, accurately stoichiometric phases. Therefore other methods such as citrate precursors are used.

Citrate Precursor Method

In this method (Figure 5), the metal ions from the starting materials such as nitrates are complexed in an aqueous solution with α - carboxylic acids such as citric acid.

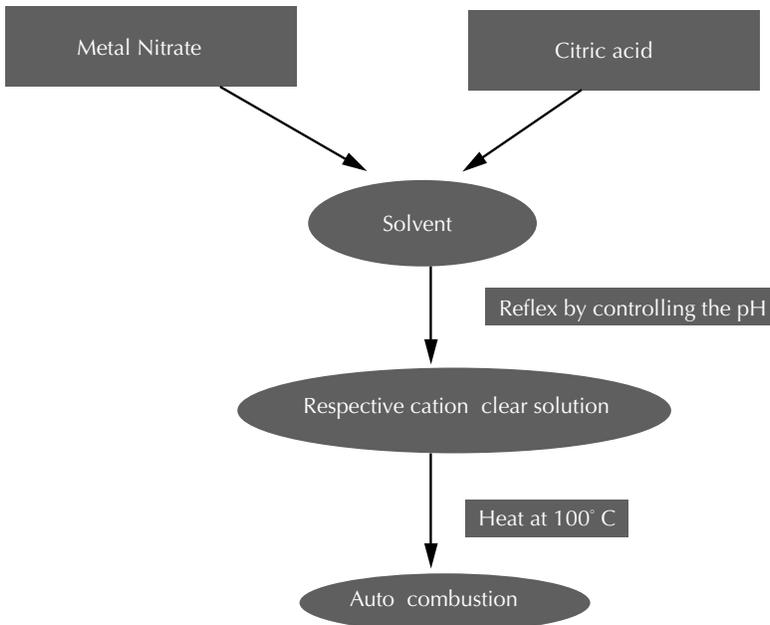


FIGURE 5 Citrate precursor method of preparing ferrites.

The ratio of metal nitrates to citric acid is taken in the ratio of 1:1 in order to make uniformity in the chelation of the metals. The pH of the solution is controlled at 7 by adding ammonium hydroxide. The pH controlled solution is refluxed at 40°C with continuous stirring using magnetic bar agitator and dried in an oven at 100°C. A highly viscous mass is then formed by the evaporation of the solution resulting from metal nitrates and citric acid. Now the citric acid which also act as a fuel provider for redox reaction provides fuel for the ignition step of the process as it is oxidized by the nitrate ions. Finally, auto-combustion or the ignition process takes place just like the eruption of a volcano giving rise to a dark brown voluminous product which is the ash-synthesized ferrite powder. This has been reported [18, 19].

The underlying idea for the reaction is that the metal nitrates react with water producing metal hydroxide and gases like nitrogen dioxide. Then the carboxylic acid functionalities from the citric acid chelant are deprotonated with ammonium hydroxide and the metal hydroxide by removing protons. This results in production of metal ions having a positive valency and carboxylic ions with negative valency together with water molecules. Finally, coordinate bonds are formed between the metal ions and carboxylate ions of the chelant to produce the metal and acid complex which is the ash-synthesized powder obtained. It is then given final sintering. Several characteristic properties of substituted lithium ferrite were prepared by this method and investigated.

1.4 MAGNETIC STUDIES

1.4.1 Superexchange Interaction in Ferromagnetic Spinel

The superexchange interaction of magnetic ion to understand the magnetic properties of oxides of transition metal was first recognized by Kramer [20] and demonstrated later by Neel [21] but the most advanced state was brought by the work of Anderson [22]. Superexchange interaction is the interaction that takes place through a passive intermediary. The mechanism of superexchange interaction can be illustrated by considering two metal ions and an oxygen ion having a purely electrovalent bond, represented by M-O-M where M are the two metal (Fe^{3+}) ions separated by an O^{2-} ion.

The metal-metal distances are sufficiently large and the orbital wave functions of the 3d electrons of Fe^{3+} ions do not overlap the next metal ion but it overlaps the neighboring oxygen ion. Therefore, the direct exchange interaction between the two Fe^{3+} ions is not possible but involves the participation of the intervening O^{2-} anion. The outer shell of the O^{2-} anion has an electronic configuration s^2p^6 . Since, the outer shell is completely filled there is no spin coupling. However, in an excited state one of the electrons from 2p shell move out bonding itself to the 3d shell of one of the neighboring metal (Fe^{3+}) cation. As a result, the oxygen ions becomes O^- with an outer electronic configuration of s^2p^5 and a resulting spin moment of one Bohr magneton μ_B parallel to the resultant spin of the metal ion involved in the interaction. These net spin of the O^- ion interact directly with neighboring magnetic ion.

The superexchange interaction has a dependence on the bond separation as well as the bond angle. With increase in the bond separation there is a decrease in the interaction. These interactions are found to be strongest when the bond angle between the two metals and oxygen ion represented as M-O-M is 180° With further decrease in bond angle the interaction decreases and reaches the minimum for an angle of 90°.

According to Neel, there are three types of superexchange interactions present in spinel ferrites—the interaction between neighboring magnetic ions located at A sites (AA interaction), the interaction between various ions in sublattices A and B (AB interaction) and the interaction between neighboring magnetic ions located at B sites (BB interaction) [20, 21]. The AA interaction is very weak because the metal oxygen distance is very large about 3.5 \AA and the angle of A-O-A is about 80° . The distance for the BB exchange interaction is reasonable, being about 2.1 \AA but the angle of B-O-B is 90° and hence the magnitude of interaction is minimum. The AB interaction, for which the distance is short $\sim 1.9 \text{ \AA}$ and the angle A-O-B is favorable, being about 125° , is the strongest of the three. The BB interaction is not, however, completely negligible and plays an important role in certain mixed ferrites like the mixed zinc ferrites. When the AA or BB interaction becomes comparable in magnitude to the AB interaction, the magnetic moments of the sublattice are arranged in a triangular form and are said to be canted. These canted magnetic moments occur because of the magnetic dilution of one of the sublattice by substituting non magnetic ions in the ferrites. Besides, non magnetic substitution, change in temperature can also lead to this competitive situation [23, 24].

1.4.2 Saturation Magnetization in Ferrites

In ferrites, the magnetization is due to the antiparallel uncompensated electron spins of the two A and B sublattices. Hence, the net magnetization is given by the difference between the magnetization of the two sublattices. The saturation magnetization occurs when all its individual magnetic domains are aligned in the direction of the applied magnetic field such that with further increase of the external field, the intrinsic magnetization within the domain increases. This saturation magnetization value is observed to change with increase in temperature. The increase in temperature destroys the magnetic ordering thereby decreasing the magnetization and leading finally to the zero magnetization which gives the Curie temperature.

Ferrite exhibiting ferrimagnetisms is governed by the superexchange interaction. According to Neel, the AB exchange interaction is stronger than the AA and BB interaction. This is because for AB interaction the cation and anion distances are small and the angle A-O-B is about 125° whereas for AA and BB interaction the angles are about 80° and 90° respectively. The saturation magnetization which is the vector sum of the two sublattices can now be written as:

$$\overrightarrow{M}_S = \overrightarrow{M}_B - \overrightarrow{M}_A$$

where M_B and M_A are the magnetizations of the B and A sublattice respectively.

The effect of magnetic interaction on the magnetic moments can be studied considering the different kind of spinel ferrite such as normal, inverse, and mixed ferrites.

1.4.3 Curie Temperature (T_C)

The T_C is the critical temperature at which the aligning effect of exchange interactions on the spins of magnetic ion is cancelled by the disordering effect of random thermal motion and the spontaneous magnetization of the ferro or ferrimagnetic material

vanishes by changing to the paramagnetic state. It is possible to attain perfect alignment of the magnetic spins of all the molecules only at 0 K.

In the case of ferromagnetic materials, the exchange interaction of neighboring electrons produces a strong effective field called the molecular field [25]. This field is responsible for the alignment of the magnetic dipoles parallel to each other. As the temperature is increased the spontaneous magnetization decreases from M_o , its value at $t = 0$ till the magnetization disappears at the point called the Curie temperature. This disappearance of magnetization at T_C is due to the fact that there is sufficient thermal energy of the lattice to overcome the interaction energy and hence the magnetic ordering is destroyed making the materials paramagnetic. In ferrimagnetic materials, the variation of magnetization with temperature may be more complicated. As in the case of ferromagnetic materials, here also the spontaneous magnetization disappears at the Curie temperature. The magnetic characteristics of a ferrimagnetic material is mostly controlled by superexchange interactions between the Fe^{3+} ions in A and B sites mediated by the oxygen anions. The strongest superexchange interaction is given by the antiparallel alignment of spins between the A and B sites. Hence, the overall strength is determined by the AB interaction which has a direct relation with the T_C [26]. This strength of the AB interaction is determined by the number of $Fe_A^{3+} - O^{2-} - Fe_B^{3+}$ linkages per magnetic ion per formula unit. Hence, the T_C depends on the number of $Fe_A^{3+} - O^{2-} - Fe_B^{3+}$ linkages per Fe^{3+} ion per formula unit.

According to the relationship given by Gilleo, the interaction energy assigned to each linkage may be written as $\frac{kT_C}{n}$, where k is the Boltzmann constant and n is the number of interactions. Therefore, if E_A and E_B are the respective energies needed to invert the spins of ions at A and B sites for a ferrite, the average thermal energy required to create absolutely non-interacting ions is given by [2]:

$$kT_C \simeq \frac{n_A}{n_A + n_B} E_A + \frac{n_B}{n_A + n_B} E_B$$

where n_A and n_B are the number of magnetic ions at A and B sites, respectively.

In a compound of ideal crystal, the chains of such linkages are infinitely long. However, the nonmagnetic ion substitution decreases the number of active linkages weakening the various exchange interactions. Thus, there is a reduction of thermal energy required to offset any spin alignment with the result that Curie temperature is reduced. The study of T_C gives an estimate of the operating temperature limit for the magnetic materials.

1.5 MÖSSBAUER STUDIES

Mössbauer spectroscopy is concerned with transition that takes place inside atomic nuclei. The incident radiation that is used is a highly monochromatic beam of gamma rays whose energy may be varied by making use of Doppler effect. The gamma rays that are used in Mössbauer spectroscopy are produced by decay of radioactive elements such as $^{57}Fe_{26}$ or $^{119}Sn_{50}$. Under certain condition of recoilless emission all of