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A REVIEW ON FERRITES – ITS CLASSIFICATION AND APPLICATIONS

K. Alamelu mangai ,
Associate Professor,Department of Physics,
Vel Tech High Tech Dr. Rangarajan Dr. Sakunthala Engg. College,
Avadi, Chennai, India.

ABSTRACT

Ferrites are the unique magnetic materials which that exhibit electrical as well as magnetic properties and hence are commercially and scientifically important magnetic material . A brief introduction to various types of ferrites materials is explained herein. The chemical composition of ferrites including spinel type, garnet type and hexagaonal type is given in this review. The most interesting applications in electronic devices High frequency devices and in biotechnology are discussed. Since its discovery in 1950, hexaferrite has an increasing degree of interest and is still growing exponentially. Hexaferrites are the extremely important material both commercially and technologically and it accounts for the bulk of the total magnetic materials manufactured globally. Hence the classification of Hexaferrite is discussed in detail in this review.

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1.INTRODUCTION

Ferrimagnetic materials or ferrite materials have incomplete cancellation of the magnetic dipoles in a domain that results in lower permanent magnetization; it is the sum of the magnetizations of the domains.

Ferrites are normally ferromagnetic- non conductive compounds of ceramics derived from iron and also from oxides of other metals. Based on the crystal structure and compositions, ferrites are classified as spinel, garnet and hexaferrite.

2.CLASSIFICATION OF FERRITES

Table 1.1 represents types of ferrites with their crystal structure, general formula and replacements. Ferrites are classified according to magnetic properties and their crystal structure.

2.1 CLASSIFICATION BASED ON MAGNETIC PROPERTIES

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

2.1.1 Soft ferrites

Soft ferrites are ferrimagnetic materials with cubic crystal structure and they are characterized by chemical formula $MO \cdot Fe_2O_3$, where M is a transition metal ionslike Iron, Nickel, Manganese or Zinc. 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,

Table 1.1 Ferrites with their structures and general formula

Sl. No	Types	Crystal structure	General formula	Replace ments
1	Spinel	Cubic	$A^{II}Fe_2O_4$	A^{II} - Mn, Zn, Ni, Mg, Co
2	Garnet	Cubic	$Ln^{III}_3Fe_5O_{12}$	Ln^{III} - Y, Sm, Eu, Gd, Tb,Dy, Ho, Er, Tm and Lu
3	Ortho ferrite	Perovskite	$Ln^{III}FeO_3$	Ln^{III} - Y, Sm, Eu, Gd, Tb,Dy, Ho, Er, Tm and Lu
4	Magnetoplumbite	Hexagonal	$A^{II}Fe_{12}O_{19}$	A^{II} - Ba, Sr, Pb

pulse, square, etc). At high frequency metallic soft magnetic materials simply cannot be used due to the eddy current losses. Therefore, soft ferrites, which are ceramic insulators, become the most desirable material for example in

telephone signal transmitters and receivers and in switch mode power supplies (referred as DC-DC converters). For such type of application the driving force to increase frequency is to allow miniaturization.

2.1.2 Hard ferrites

Permanent ferrite magnets are made up of hard ferrites, which have a high coercivity and high remenance after magnetization.

These ferrites are composed of iron and barium / strontium oxides. They conduct magnetic flux In a magnetically saturated state and they have a high magnetic permeability. Because of this property these ceramics to store stronger magnetic fields than iron . Ferrites are cheap, and are widely used in refrigerator magnets and other household products ..

The hexagonalferrite structure is found in both $BaO \cdot_6 Fe_2O_3$ and $SrO \cdot_6 Fe_2O_3$, but Sr-M hexaferritehas slightly superior magnetic properties.

2.1.3 Spinel ferrites

Spinel ferrite crystallizes in the cubic structure. The spinel lattice is composed of a close-packed oxygen anions arrangement in which 32 oxygen ions form the unit cell (the smallest repeating unit in the crystal network).These anions are packed in a face centred cubic (FCC) arrangement leaving two kinds of spaces between anions: tetrahedrally coordinated sites (A),surrounded by four nearest oxygen atoms, and octahedrally coordinated sites (B), surrounded by six nearest neighbor oxygen atoms (Figure 1.3).

There are total 64 tetrahedral sites and 32 octahedral sites in the unit cell, of which only 8 tetrahedral sites and 16 octahedral sites are occupied, resulting ina structure that is electrically neutral (Pieper et al 2002).

Although most spinel ferrites are cubic, there are some exceptions likeCu Fe_2O_4 that can have tetragonal unit cell symmetry if the sample is slowly cooled from high temperatures. There exists a super exchange interaction between the cationsoccupied in different interstitial sites through oxygen anion
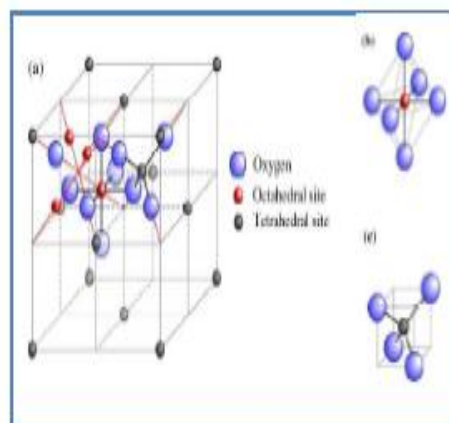
Figure 1.3 (a) Spinel structure, (b) octahedral interstice (B site: 32 per unit cell,16 occupied), and (c) tetrahedral interstice (A site: 64 per unit cell, 8 occupied)
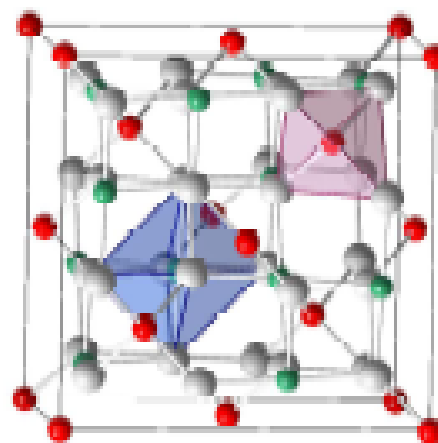
Figure 1.4 Spinel unit cell structure

2.1.4 Garnet ferrites

The garnet structure is one of the most complicated crystal structures and it is difficult to draw a two dimensional representation that shows clearly all theions (160) in the unit cell. For simplicity, only an octant of a garnet structure that shows just the cation positions is shown in Figure 1.5.

The garnet structure iscomposed of a combination of octahedral (trivalent cation surrounded by six oxygen ions), tetrahedral (trivalent cations surrounded by four oxygen ions), and 12-sidedpolyhedral - dodecahedral - (trivalent cations surrounded by 8 oxygen atoms) sites, the orientations of which are shown in Figure 1.6 (a) (Collomb et al 1986,

Handley 2000).

The chemical formula for garnets is $3Me_2O_3 \cdot 5Fe_2O_3$ where Me represents the trivalent rare earth ions like nonmagnetic yttrium or a magnetic rare earth such as from lanthanum through ytterbium (Valenzuela 2012). Yttrium based garnets are used in microwave devices and thin mono crystalline films of complex garnets have been developed for bubble domain memory devices.
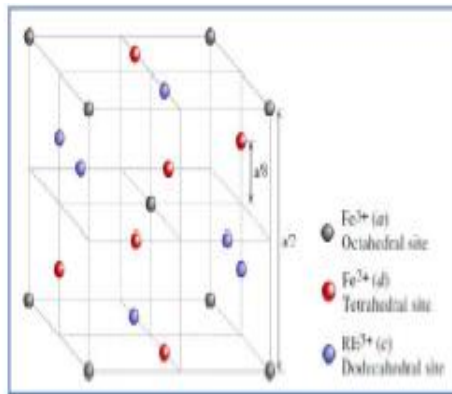

Figure 1.5 Schematic representation of an 'octant' of a garnet crystal structure (lattice constant 'a') showing cation positions.
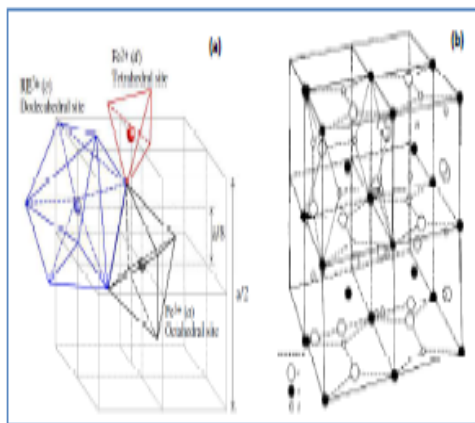

Figure 1.6 (a) An 'octant' of a garnet crystal structure (b) Unit cell of a rare earth garnetFigure 1.6 (b) shows a unit cell of rare earth garnet.

2.1.5 Ortho ferrite structure

Rare earth ortho ferrites are classified as ferrites, although they are cantedantiferromagnets.

The magnetic oxides with perovskite structure,

which have been studied by Jonker and Van Santen (Kools et al. 2002) are an exception in the group of oxides. The perovskite structure is shown schematically in Figure 1.7. Large divalent or tri valent ions (A) occupy the corners of a cube and small trivalent or tetravalent metal ions (B)occupy the centre of the cube.

The oxygen ions are situated centrally on the faces of the cube. The general chemical formula is ABO_3, where A represents yttrium or a rare-earth.
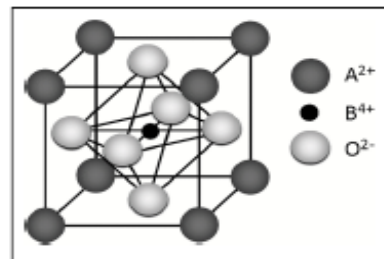

Figure 1.7 A Perovskite structure of an orthoferrite

The magnetic structure inside of a sublattice is usually collinearferromagnetic, but the different sublattices are coupled anti-ferro magnetically. Due to the different number of magnetic ions in differen tmagnetic moment, gives rise to ferrimagnetism. The nature of the superexchangeinteraction depends not only on the type of the magnetic ion, but rather strongly onthe bond length and bonding angle. This makes it possible type of the super exchange interaction
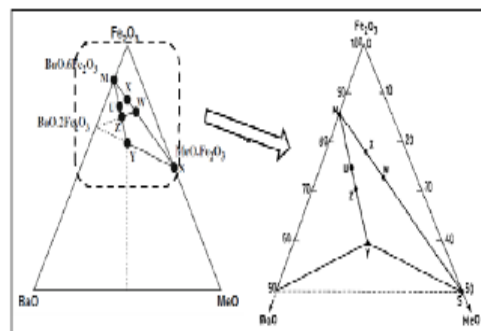
2.2.Hexaferrites

Figure 1.8 Chemical compositional BaO-MeO- Fe_2O_3 ternary phase diagram showing how the different hexagonal ferrites are derived

Hexaferrite possesses magneto plumbite

structure in hexagonal. Thus, it has a major preferred axis called the'c'-axis and a minor axis called thea'-axis. The preferred direction is used as a permanent magnet material.

The oxygen ions are closely packed as they are in the spinel structure but there are oxygen layers which now include the Ba_{2+}, Sr_{2+} or Pb_{2+} ions which have about the same ionic radii as the oxygen ions and therefore can replace them in the lattice.

2.2..2 CLASSIFICATION OF HEXAFERRITES

Several related ferromagnetic oxides are also available all of which can be derived by combining the ferrite spinel(MeO· Fe_2O_3)and ferroxdure (BaO·$_6$- Fe_2O_3) using the chemical composition diagram shown in Figure 1.8. The same with chemical formula for each type, namely M,Y, W, Z, X and U, is given in Table 1.2 (Fiorillo 2010).

Hexaferrites are classified according to magnetic properties and their crystal structure. They are explained as follows:

(i) M-type hexaferrite: Magneto plumbite-structured ferrites having a generic formulaMO·6Fe_2O_3, where M represents divalent ions such as Ba_{2+}, Sr_{2+}, or Pb_{2+}. It hashexagonal structure composed of stacked spinel ionic layers with interspaced ionic layers of M^{2+}, O^{2-} , and Fe. These types of oxide ferrites have extensive magneto crystallineanisotropy due to their low crystal symmetry. The magnetoplumbite contains a total of ten layers, two of which contain the Ba^{2+}: four layers of fou roxygen ions each; followed by a layer of three oxygen ions and one Ba^{2+} ion; again followed by four layers of four oxygen as having ions each; and another layer containing three oxygen and one Ba^{2+} ion but situated diametrically opposite to theBa^{2+} ion in the previous layer containing Ba^{2+}. The Fe^{3+} ions are located in the interstices of these ten layers. There are octahedral and tetrahedral sites plus one more type not found in the spinel structure in which the metal ion is surrounded by 5oxygen ions forming a trigonal bi-pyramid in the same layer as the Ba^{2+} ion.

Table 1.2 Hexaferrite types with their chemical formulae, composition and stacking order

| Sl. No	Hexaferrite Type	Composition	Stacking Order#
1	S-Spinel	2MeO·2Fe_2O_3	S
2	M	BaO.6Fe_2O_3	RSR*S*
3	Y	2BaO·2MeO·6 Fe_2O_3	TSTST
4	W	BaO · 2MeO · 8 Fe_2O_3	RSSR*S*S*
5	Z	3BaO · 2MeO · 12 Fe_2O_3	RSTSR*S*T*S*
6	X	2BaO·2MeO·14 Fe_2O_3	RSR*S*S*
7	U	4BaO · 2MeO · 18 Fe_2O_3	RSR*S*T*S*

#Sub-units for stacking order, using, $S = Fe_6O_8$ (spinel), $R = BaFe_6O_{11}$ (hexagonal), and $T = Ba_2Fe_8O_{14}$ (hexagonal). The asterix (*) indicates that the corresponding sub-unit is rotated 180 º around the hexagonal axis.

Figure 1.9 (a) shows the schematic crystal structure of M-type hexaferrites$SrFe_{12}O_{19}$/ $BaFe_{12}O_{19}$. The M-type ferrite crystallizes in a hexagonal structure with 64ions per unit cell on 11 different symmetry sites (P63/mmc space group). The structure of M-type hexagonal is stacked alternatively by spinel ($S = Fe_6O_8^{2+}$) and hexagonal($R = MFe_6O_{11}^{2-}$) layers. The O^{2-} ions exist as close-packed layers, with M^{2+} substituting for an O^{2-} in the hexagonal layer. The three parallel (2a, 12k and 2b) and two anti-parallel (4f1 and 4f2) sub-lattices, which are coupled by super exchange interactions through the O^{2-} ions, form the ferrimagnetic structure (Fiorillo et al 2010). A schematic M type structural representation and the surroundings of five Fe^{3+} sites are shown in are shown in Figure 1.9 (b) by Collomb et al. (Liua et al. 2006)

The 24 Fe^{3+} atoms are distributed over five distinct sites: three octahedral sites(12k, 2a and 4f2), one tetrahedral (4f1) site and one hexahedral (trigonal bipyramidal)site (2b).The arrows on Fe ions represent the direction of spin polarization.

The unit cell contains a total of 38 O^{2-} ions, 2 Sr^{2+} ions, and 24 Fe^{3+} ions. Fe^{3+} ions in 12k, 2a,and 2b sites (16 total per unit cell) have their spins up, while the Fe3+ ions in 4f1 and4f2 sites (8 total per unit cell) have their spins down, which results in a net total of 8spins up, and therefore, a total moment of 8 x 5 μB = 40 μB per unit cell that contains two Sr^{2+} ions. The asterix (*) indicates that the corresponding sub-unit is rotated 180°around the hexagonal axis.
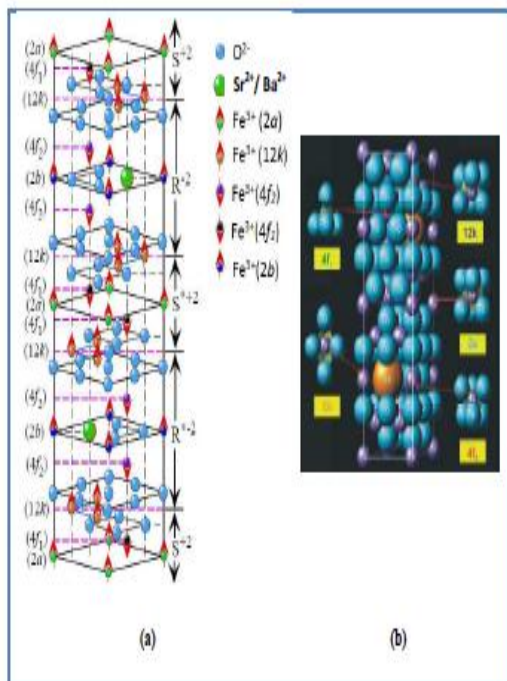

Figure 1.9 (a) The crystal structure of M-type hexagonal and (b) BaFe$_{12}$O$_{19}$ along with five Fe sites with their surroundings.

Strontium ferrite is almost identical to BaFe$_{12}$O$_{19}$ in its crystallographic structure and magnetic properties, except that the sintered magnets generally have higher coercivity. The magnetic moments of the iron ions (Fe$_{3+}$) which lie along the c axis are coupled to each other by a super exchange interaction. The angle between the ferric cations and oxygen in Fe-O-Fe bonds determines their anti-ferromagnetism (i.e. ,larger exchange for larger angles). The ferromagnetic resonance (FMR) line width for a single crystal is reported to range from 10 to 20 O$_e$(Musat et al. 2010).

(ii) Y-type hexaferrite: The Me$_2$Y (Y-type) hexaferrite contains different combination of barium layers and spinel blocks. The unit cell

is composed of these quence STSTST including three formula units. In Y-type structure, tetrahedral and octahedral sites are occupied by metal ions. However, the Me$_2$Y has a preferred planewhich is perpendicular to the c-axis in which the magnetization can move freely soMe$_2$Y hexaferrites cannot be used as a permanent magnets. Figure 1.11 (b) shows the unit cell cross-section of Y-type hexaferrite and Figure 1.10 (a) represents the polyhedra of Y-type.
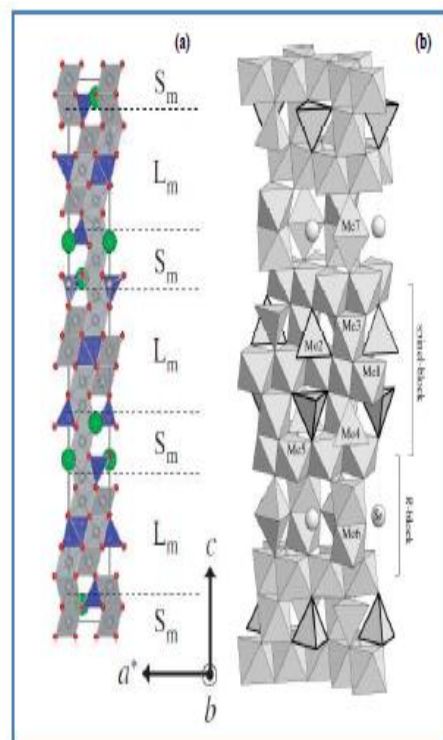
Figure 1.10 (a) Y-type hexaferrite structure and (b) A polyhedral representation of the SrZnCoFe$_{16}$O$_{27}$ W-type hexagonal ferrite. Me1 – Me7 denote the different polyhedral

(iii) W-Type hexaferrite: The Me$_2$W (W-type) hexaferrite exhibits a magnetic uniaxial anisotropy along the c-axis of the hexagonal structure as in the case of the M-type hexaferrite. The unit cell of W-type is composed of the sequence RSSR*S*S*.There is a 180° rotation between R-R* and S-S*

blocks around c-axis. The W structure consists of one Ba containing layer for every seventh oxygen layer of thespinel structure and is thus closely related to the M structure. Substitution of different combinations of divalent metal

ions paves the way for changing the saturation magnetization and Néel temperature of the W hexaferrite. Figure 1.10 (b) showspolyhedral representation of W-type hexaferrite.

(iv) Z-type hexaferrite: Me₂Z (Z-type) being the sum of M and Y compounds, it is somewhat different in that the M portion attempts to cause a preferential direction along the c-axis while the Y portion attempts to cause planar anisotropy in the plane perpendicular to the c-axis. Figure 1.11 (c) shows unit cell cross sections of Z-type hexaferrites.

(v) X-type hexaferrite: X-type hexaferrites constructed as stack of hexagona lR-block and spinel S-block along the hexagonal c-axis with a model as RSR*S*S*,with the (*) indicating the rotation of corresponding block by 180 ° around thec-axis. The structure of X-type compound is closely related to that of M and W type. The X-type hexaferrite can be constructed by X = 2 M + S as seen from Figure 1.8.

(vi) U-type hexaferrite: U-type hexaferrite having general formula $Ba_4Me_2Fe_{36}O_{60}$with Me a bivalent transition metal ions, is very difficult to prepare in single phase condition owing to their complex crystalline structure. It can be constructed byU = 2 M + Y as indicated in Table 1.1.Hexaferrites are widely used as permanent magnets and are characterized by possessing a high coercivity (Hadley 1999). Their general formula is $A^{2+}Fe_{12}^{3+}O_{19}$ where A can be Ba, Sr, or Pb. The hexaferrite lattice is similar to the spinel structure, with the oxygen ions closely packed, but some layers include metal ions, which have practically the same ionic radii as the oxygen ions. This lattice has three different sites occupied by metals:tetrahedral, octahedral, and trigonal bi pyramid (surrounded by five oxygen ions).
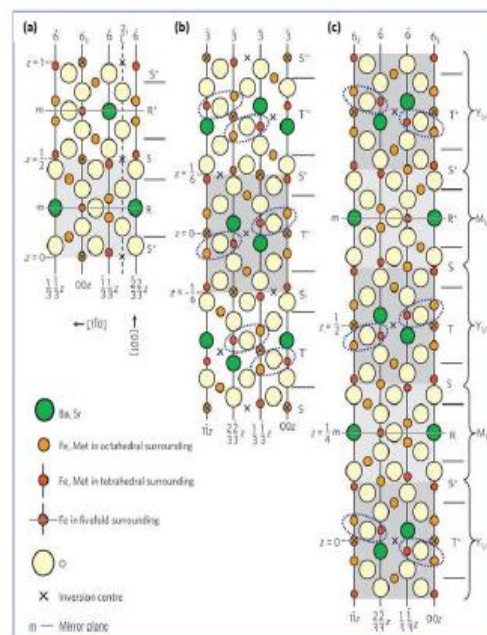

Figure 1.11The unit cell cross-sections of (a) M-type, (b) Y-type and (c) Z-type hexaferrites

3.APPLICATION OF FERRITES

The applications of ferrites is mainly based upon their basic properties of ferrites such as good chemical stability, pronounced saturation magnetization, a high electrical resistivity, and low electrical losses. Ferrites can be prepared by many methods, and the viability to prepare a large number of solid solutions opens the means to modify their properties for many required applications.

The prospects of preparing ferrite nanoparticles has opened a new research field, with innovative applications in the field of electronics and biotechnology (Miclea et al. 2005). Ferrite magnets have the advantages of simple production technology and low cost. Ferrite magnets have modest magnetic performance compared to the other main commercial magnet materials.
Hexagonal ferrites such as $BaFe_{12}O_{19}$, SrFe12O19 are currently employed in many different sectors as permanent magnets. The main application for high-grade ferrite magnets is as segments in various DC motors for the automotive industry (Boon et al 2012, Kumbhar et al. 2010 &Tsakaloudi 2007).

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3.1 Electronic devices

There are tremendous applications in electrical and electronic sector. Some of the applications are listed below:

- In power supplies ferrites are applied in input filters, as inductors for resonant circuits and as output chokes.

- Primarily ferrites are used as inductive components in electronic circuits like voltage-controlled oscillators, low noise amplifiers and impedance matching networks,

- Sensors based on nickel ferrites ($Ni_{1-x}Zn_xFe_2O_4$ with x = 1 to 0.5) / lead zirconate-titanate ($PbZr_{0.52}Ti_{0.48}O_3$) have shown excellent performance.

- Hexaferrites represent an interesting material for EMI (Electromagnetic interference) suppressor components.

- Ferrite has been extensively used in many electronic chip devices because of high permeability in MHz ranges, high electrical resistivity and excellent chemical stability.

- Spinel ferrites, MFe_2O_4 (M= Ni^{2+}, Co^{2+}, Cu^{2+} etc.) are the important materials in electronic material industries which include antenna rod, transformer core, recording head, loading coil, memory and microwave devices etc.

- Due to their high rate of change of permeability with temperature, soft ferrites of MnCu, NiZn and MnZn are used for magnetic temperature sensors.

SMPS (switching-mode power supply)- transformer is normally made with magnetic materials, like Mn-Zn ferrite and Co-type amorphous soft magnetic materials (S. Chang et al. 2012, U. Ozguri et al. 2009 & V.G. Harris et al. 2009).

3.2 Microwave devices

Study on the Microwave absorbers is the recent topic of interest due to increased use in aircraft, ship, microwave darkroom, anti-electromagnetic interference coating, microwave thermal seed materials, etc.

Ferrites are the choice materials for microwave applications. Barium hexaferrites, which possess large saturation magnetization and high natural resonance frequency, have been well known as special kinds of absorbing materials.

Ferrite nanoparticles in combination with carbon nanotubes ($CoFe2O_4$ spinel nanocomposite) can efficiently absorb microwave radiation (T. Tanaka et al. 2009 & M. Tada et al. 2009). 1.5.4.3 High frequency devices Eddy current losses are usually high and increase with the square of the frequency In devices for high frequency applications.

These losses are inversely proportional to the resistivity. Therefore the high resistivity of the ferrites is the major factor for its wide application in high frequency magnetic components such as telecommunications and radar systems.

NiZn ferrite has attracted a great deal of interest due its promising electromagnetic properties for application in high frequency devices. (J. Giria et al. 2008).

3.3 Bioscience In recent years, nanomagnetic particles have generated a lot of attention in the biomedical applications like MRI (Magnetic Resonance Imaging) contrast enhancement, magnetic separation, hyperthermia, tissue repair, immunoassays, and detoxification of biological fluids, drug delivery, and cell separation techniques.

Among the different magnetic oxides, Fe_3O_4 and á-Fe_2O_3 particles have been extensively studied as they are known to be biocompatible within certain threshold limits. Thermal energy from hysteresis loss of ferrites is suitable for heating of specific tissues or organs. This principle is used in for treatment of cancer. The unique characteristics of spinel ferrite nanoparticles such as chemical stability, appropriate self-heating temperature-rising characteristics, and a high biological compatibility place this as a promising materials for hyperthermia.

Magnetic nanoparticles in the form of ferrofluid is most suitable for biological applications is ferrofluid. $Mn_xZn_{1-x}Fe_2O_4$ ferrites are among the most temperature sensitive mixed ferrites and are used to prepare magnetic fluids in polar and non-polar solvents (Bean, Livingston 1959, Dino Fiorani 2005 &Gueron et al. 1999).

4. CONCLUSION

Ferrites are ceramic materials and suitable for the high-frequency operation Ferrites are highly developed prominent materials with suitable for applications ranging from hard magnets to magnetic recording and to microwave devices. The advances in applications and fabrication technologies in the recent years is enormous

Though bulk ferrites continue to be the main magnetic materials for various applications, nanostructured ferrites show a remarkable choice for applications in significantly wider fields. The applications of nanostructured ferrites will be reviewed in our next article.

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