1.1 Introduction of Ferrites

Ferrites are ceramic ferromagnetic materials, which are composed of ferric oxide, \((\alpha - \text{Fe}_2\text{O}_3\text{ hematite})\) and have been considered as highly important electronic materials for more than half century. Ferrites, being mixed oxides of high resistivity, are members of semiconductor family which are made by sintering a mixture of various metallic oxides. Their crystal structure is cubic in shape and belongs to that of mineral spinel \((\text{MgAl}_2\text{O}_4)\). The saturation magnetization of ferrites is less than that of ferromagnetic alloys. They are applicable at higher frequency, lower price, greater heat resistance and higher corrosion resistance. Ferrites are ferromagnetic oxides with dielectric and magnetic properties that are useful for RF and microwave applications [1,3]. Ferrite materials are considered as an important and essential materials for the further development of electronics, and it is believed that the production of ferrites will increase year by year as their applications become more diverse. The period of 35 years from 1935-1970 can be referred to as the golden age of ferrites – the time during which the greatest development was seen in science and technology of ferrites, one should not consider from this statement that the ferrite research and development dwindled after the golden age, but the situation is exactly reverse. The soft and hard ferrites as well as ferrites for xerographic printing have experienced an increase in output [4].

Ferrites crystallizes in three different crystal types namely spinel, garnet, and hexaferrites.

(i) Spinel: The chemical formula of ferrites possessing the structure of mineral spinel, \(
\text{MgAl}_2\text{O}_4\), is \(\text{MeFe}_2\text{O}_4\), where \(\text{Me}\) is a divalent metal ion with ionic radius 0.6 to 1 Å. The trivalent iron ion in \(\text{MeFe}_2\text{O}_4\) can be completely or partially replaced by another trivalent ion like \(\text{Al}^{+3}\) or \(\text{Cr}^{+3}\). The unit cell of the spinel structure contains 8 molecules of \(\text{MeFe}_2\text{O}_4\). In the spinel structure 8 tetrahedral (A site) and 16 octahedral (B site) sites are occupied by bivalent metal ions.
(ii) Garnet: The chemical composition in garnet is $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. By substituting $\text{Y}^{3+} + \text{Al}^{3+}$ for $\text{Mn}^{2+} + \text{Si}^{4+}$ the first silicon free garnet $\text{Y}_3\text{Al}_5\text{O}_{12}$ was obtained. The iron ions, having the smallest radii, occupy tetrahedral ($\text{Fe}^{3+}$) and octahedral ($\text{Fe}^{2+}$) sites similar to spinel structure. The tetrahedral and octahedral sites occurring in the garnet structure are occupied by the metal ions. The Yttrium ion can be substituted for an oxygen ion, each of which is surrounded by 12 oxygen ions.

(ii) Hexaferrites: Hexaferrites are the magnetic oxide materials and possess 'magnetoplumbite' structure. The symmetry is hexagonal. It has a major preferred axis called the c-axis and minor axis called the a-axis. The packing of oxygen ions are similar to spinel structure but there are oxygen layers which can include $\text{Ba}^{2+}$, $\text{Sr}^{2+}$ and $\text{Pb}^{2+}$ having same radii as that of oxygen. The hexagonal close packed (HCP) structure is represented schematically in Fig. (1.1).

![Hexagonal packed structure](image)

Fig. (1.1): The hexagonal packed structure

In hexagonal closed packed structure, spheres can be arranged in a single closed packed layer by placing sphere in contact with six others. The second layer $B$ can be placed in the interstices formed by $A$, again a third layer similar to that of the first layer whose centre coincides with the centres of first layer can be added. When the centres of the first layer spheres and those of the third layer spheres are joined, a right prism having a regular hexagon for its base is obtained. Therefore, the unit cell of this structure is a hexagon. In the view of this, the ABAB pattern...
packing is called hexagonal close packing and the resulting three dimensional structure, is known as hexagonal close packed structure.

The ferromagnetic oxides consists of closely packed oxygen ions. The structures can be built up from sections having a cubic and a hexagonal structure. In barium hexaferrites some oxygen (1.32 Å) ions are replaced by barium (1.43 Å) ions, which are approximately of the same size as oxygen ions. The atoms in hexagonal closed structure attains lower energy and a more stable condition. The co-ordination number of hexagonal structure is 12.

1.2 Classification of hexagonal ferrites

Hexagonal ferrites are divided into six different types: M(AFe12O19), W(AME2Fe16O27), X(A2Me2Fe28O46), Y(A2Me2Fe12O22), Z(A3Me2Fe24O41) and U(A4Me2Fe36O60), where A = Ba, La, Sr and Me = a bivalent transition metal ion [5]. The crystal structure of W-type hexagonal ferrite considered as superposition of R (block with one barium ion, one metal ion and oxygen ions) and S (block with oxygen and metal ions) block along the hexagonal C-axis. The crystal structure of W-type hexaferrite can be built up from spinel blocks of two oxygen layers being S and S*, which are connected by a block R containing the barium ion, where R is a three oxygen layer block with composition Fe6O8. M-type hexaferrite has a crystallographic structure RSR*S*, where * means the respective block is turned 180° around the hexagonal axis. In the M-structure the spinel block consists of two or more O2 layers [7]. The Y structure can be built up from spinel STSTS blocks of two oxygen layers. The structure is composed of alternating S and T blocks. In Y structure only tetrahedral and octahedral sites are occupied by metal ions. The Z structure is the sum of M and the Y structure i.e R*STSRS*. Z structure belongs to the family of planar hexagonal ferrites with a high permeability at GHz frequency.
1.3 Applications of hexaferrites

Hexaferrites are very attractive materials for high frequency circuits and operating devices. Hexaferrites are used at microwave frequencies. At microwave frequencies, they exhibit non-reciprocal properties i.e the attenuation and phase shift of microwaves propagating through them have different values for the two opposite directions of propagation in a wave guide. They are widely used as permanent magnets, high density magnetic recording media and microwave devices. Barium hexagonal ferrites are used for high density, overcoat free, contact or semi contact recording media [6]. On account of their superior chemical stability, mechanical hardness, excellent corrosion and wear resistance, low level of media noise, they are suitable for rigid disk media without protective and lubricant layers. Due to large magneto crystalline anisotropy and strong dependence of the orientation of easy axis on the microstructure, they have potential for application in both perpendicular and longitudinal magnetic recording media [7,8,9]. W-type hexaferrite is a very useful material for home appliances, electronic products, communication equipments and data processing devices due to its unique electrical and magnetic properties. M-type barium hexaferrite is a high performance permanent magnetic material, due to its large magnetocrystalline anisotropy, high Curie temperature, large magnetization, excellent chemical stability and corrosion resistance [10,11,12]. However, the structural, magnetic and electrical properties of hexaferrite depends on many factors like method of preparation, sintering temperature, heat treatment, type and amount of substitution, etc [13 – 17]. Several papers describe [18,19,20] ferrite as very structure sensitive material; its properties depends upon the manufacturing process.
Mg-Zn hexaferrite [21], prepared by conventional ceramic route shows the higher loss tangent. The preparation of Ba-Zn hexaferrite by conventional ceramic route, requires sintering temperature 1300°C for 20 hours, the dielectric loss tangent of present material has been reported about 2.00 [22], Ba-Ti [23], Zn-Co [24], Zn-Ti [25,26], Ti-Co [27] have been subject of studies because of their magnetic properties resulting from particular configuration of cations in the lattices. However, different replacements of Fe$^{3+}$ in barium hexaferrite with only one cation of La, Si, Ga, Bi, Al has also been studied in detail. Recently Co-Ti substituted M type and W type barium ferrites have been investigated intensively because these materials are useful as the active ingredient in perpendicular and high density magnetic recording media [28-32]. A series of W type hexaferrites with the composition BaCo$_{2}$,$_{X}$Ni$_{x}$Fe$_{16}$O$_{27}$ and BaZn$_{2-x}$Mg$_{x}$Fe$_{16}$O$_{27}$ were studied using a ceramic technique. The dielectric behavior and conduction mechanism are studied in detail. It was found that the conductivity increases as the replacement of Co$^{2+}$ ion by Ni$^{2+}$ ion [33-35]. Microwave characterization of (Co-Zn) to W type Barium hexagonal ferrite particles were studied by Nie et al. [36]. Non magnetic zinc substituted BaZn$_{2-x}$Co$_{x}$Fe$_{16}$O$_{27}$ and Titanium substituted Ba(Co-Ti)$_{x}$Fe$_{12-2x}$O$_{19}$ nano crystalline powders were synthesized by Wang et al. [37] using a Stearic acid gel method. Very few workers have concentrated [38] on the study of the electrical and magnetic properties of rare earth substituted Ba-W hexaferrite. So far no attempt has been made to study the change in structural magnetic and dielectric properties of BaCa$_{2}$Fe$_{16}$O$_{27}$ Cobalt substituted BaCo$_{x}$Ca$_{2-x}$Fe$_{16}$O$_{27}$, BaMg$_{2}$Fe$_{10}$O$_{19}$, BaCa$_{2}$Fe$_{10}$O$_{19}$ hexaferrites at various temperature.

The lack of information about W-type allows one to start systematic studies (structural, thermal, dielectric and magnetic properties) of Barium – Calcium hexaferrite (BaCa$_{2}$Fe$_{16}$O$_{27}$). The effect of cobalt
substitution, temperature and surfactant on barium-calcium hexaferrite is studied. The effect of temperature and surfactant on M-type hexaferrites $\text{BaMg}_2\text{Fe}_{10}\text{O}_{19}$, $\text{BaCa}_2\text{Fe}_{10}\text{O}_{19}$ is studied.

Various experimental techniques have been proposed in order to prepare barium hexaferrite powders with the desired particle size, morphology and homogeneity. The technique includes ceramic, glass ceramic, chemical co-precipitation [39,40], low temperature combustion [41], sol-gel [42], mechanical alloying [43,44], solid state reaction [45], microemulsion [46,47] etc. The classical ceramic technique requires higher calcination temperatures (~1300°C). High reaction temperatures induce sintering and coagulation of particles, so the coercive forces of the materials prepared by this method usually are far below the theoretically calculated value [48]. The chemical co-precipitation is one of the simplest technique to prepare fine hexaferrite particles, resultant particles are inhomogeneous, hence an additional milling procedure is required. Literature survey reveals that Stearic acid gel method is a versatile technique to obtain ultrafine homogeneous barium calcium hexaferrite particles [37]. In sol-gel technique the annealing temperature required for crystallization is lower. The cost for preparation is less as compared to other techniques.

Less information in literature on the structural, magnetic and electrical properties of Barium-calcium hexaferrite insisted author to study the effects of temperature, surfactant and cobalt doping in barium calcium hexaferrite. Several parameters like calcinations temperature, method of preparation, preparation time effect the structure of the hexaferrite. The conventional preparation requires long time for the phase formation. Author has tried to prepare barium hexaferrite powder under various heat treatment condition and decrease the heating time for preparation by using a microwave heating.
References


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