Investigation of Rare Earth Element Inclusion on the Structural and Magnetic Properties of Barium Ferrites

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1 Introduction

Ferromagnetic oxide or ferrite is an expression that is contributed to the stuff containing oxides of metal and iron both as their mainstay [1]. Ferrites are mostly dark gray or black in their physical appearance and are also very hard and brittle. They are used thoroughly in various electric and magnetic areas as permanent magnets. Ferrites have various advantages such as wide frequency range (10 kHz to 50 MHz) [2]. They are highly resistible and temperature stable [2]. Moreover, ferrites are available at very low and reasonable cost which is one of the reasons that they are proved as commercially effective ceramic materials. Ferrite cores are widely used in toroidal inductors, cores of transformers, quality filters, transducers, memory chips and other very high operating devices [3]. Due to their low electrical conductivity and ohmic losses, they prevent eddy currents [1].

A lot of magnetic materials shows electromagnetic wave absorption owes to magnetic losses, but ferrites have been found to show considerably less losses at ferromagnetic resonance [3]. Below Curie temperature, ferromagnetic oxides manifest high-quality magnetic properties along with high intrinsic resistivity [2]. They are also used in the field of telecommunication, low-level applications and electromagnetic interference (EMI) suppression.

In addition to magnetic properties, dielectric properties are also revealed by ferrites. Ferrites are extensively owned by variety of electronic appliances. Due to their relevant conductivity, they work as electrodes in areas like chromium plating. Ferrites retaining DC resistivity of the value 10^9 or larger acquire very shallow losses which are not up to the mark of satisfying the needs for microwave applications.

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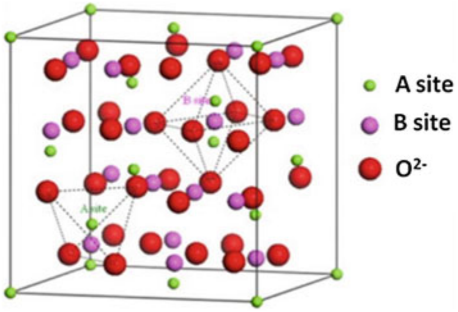


Fig. 1 Structure of spinel ferrites

Ferrites are of two types (hard ferrites and soft ferrites), both having their own advantages. Hard ferrites are also known as ceramic magnets. Hard ferrites possess high coercivity and high remanence and are mainly used in small electric motors, loudspeakers, etc. The greatest magnetic field achieved by them is nearly 0.35 T [2].

Soft ferrites possess low coercivity; hence, they can alter their magnetization easily. They are worn by switched-mode power supply (SMPS) because of their low losses at high frequencies [2]. They are quite helpful in microwave applications, radio frequency circuits, rod antennas, high-frequency digital tapes, etc.

On the basis of the crystal structure, ferrites can be divided into different categories that are spinel ferrites, hexagonal ferrites and garnet ferrites.

Spinel ferrites are the ionic compounds whose physical and chemical effects can be dogged by the cation concentration at the tetrahedral and octahedral sites. Spinel structure (Fig. 1) is closed packed layout of oxygen atoms. Smallest repeating unit of spinel ferrites is made up of 32 oxygen ions [4].

Garnet ferrites have cubic symmetry as shown in Fig. 2. There are three types of cation sites, i.e., tetrahedral (fourfold), octahedral (sixfold) and dodecahedral (eightfold). They have large importance in the field of nanofluids, color imaging and electromagnetic shielding materials [4].

Hexagonal structure of ferrites known as hexaferrites tends to have crystalline structure due to close packing of oxygen ion layers. Their structure can be portrayed on the basis of fundamental structural blocks that are S, R and T [4].

But among all these types of ferrites, hexaferrites are in spotlight as they have emerged gracefully for vast scientific and technological advancement. Hexagonal

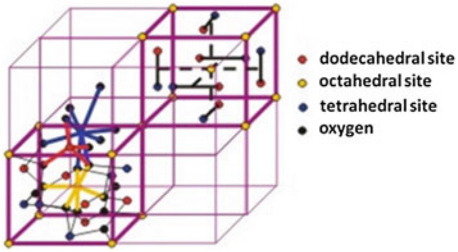


Fig. 2 Structure of garnet ferrites

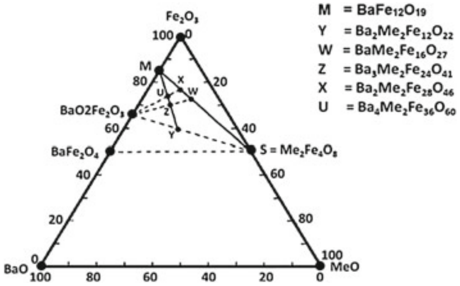


Fig. 3 Composition of hexagonal ferrites

structure of ferrites is best known for their huge role in microwave applications and in magnetic recording media due to their marvelous coercivity, Curie temperature, saturation magnetization, uniaxial magneto-crystalline anisotropy [5, 6]. Because of enormous magneto-crystalline anisotropy and chemical stability of hexaferrites, they are evaluated as preferable electromagnetic absorber in GHz frequencies [7, 8]. Hexagonal ferrites are considered to have self-biasing nature and narrow ferromagnetic resonance line width [6]. Figure 3 shows composition of hexagonal ferrites.

These ferrites are difficult to be replaced as they are comparably best magnetic material than others because they are relatively inexpensive and more stable. Spinel ferrites work under the range of 3 GHz, whereas the application range of hexagonal ferrites is felicitous for whole gigahertz zone because of their intrinsic anisotropy conduct [4].

The classification of hexagonal ferrites can be done further on the account of their chemical configuration.

That can be given as follows:

- M-type: [$BaFe_{12}O_{19}$]
- Y-type: [$Ba_2Me_2Fe_{12}O_{22}$]
- W-type: [$BaMe_2Fe_{16}O_{27}$]
- Z-type: [$Ba_3Me_2Fe_{24}O_{41}$]
- X-type: [$Ba_2Me_2Fe_{28}O_{46}$]
- U-type: [$Ba_4Me_2Fe_{36}O_{60}$]

M-type hexagonal ferrites—M-type hexaferrites ($MeFe_{12}O_{19}$) are cheaper to produce by using different methods for synthesis. They possess high electrical resistivity and intense magnetic uniaxial anisotropy across the c-axis. Saturation magnetization of M-type hexaferrites is low than the existing alloy magnets. Various features like high coercive force and chemical stability make these ferrites excellent permanent magnets [9].

Y-type hexagonal ferrites—These ferrites have acquired much more attention due to its multiferroic qualities [9]. Standard formula for Y-type hexagonal ferrites will be given as ($A_2Me_2Fe_{12}O_{22}$) where A = Sr^{2+}, Ba^{2+}, Pb^{2+}, La^{2+} and Me = bivalent transition metal. In Y-type hexagonal structure, two tetrahedral sites and four octahedral sites inhabited small cations [10]. These ferrites are handed down in electronic transmissions and microwave elements [9]. Different properties of Y-type hexaferrites can be affected by different factors such as synthesis methods, amount of substitution, sintering temperature and time and chemical composition.

W-type hexagonal ferrites—These ferrites have general formula $AMe_2Fe_{16}O_{27.}$ These ferrites are hard magnetic materials and can be used effectively as nonconductive permanent magnets and in microwave region. Like M-type hexagonal ferrites, they also show uniaxial anisotropy along c-axis [9], but saturation magnetization possessed by W-type hexaferrites is relatively more than that of M-type hexaferrites.

Z-type hexagonal ferrites—Chemical framework of Z-type hexagonal ferrites is $A_3Me_2Fe_{24}O_{41}$ where $A = Pb^{2+}$, Ba^{2+}, La^{2+}, Sr^{2+}. The Z-type hexaferrites are found generally to be the sum of M-type and Y-type units of hexagonal ferrites. They are of great importance in radar-absorbing materials (RAMs) [9].

X-type hexagonal ferrites—These types of ferrites were known near about 50 years ago. Standard formula for X-type hexagonal ferrites is $A_2Me_2Fe_{28}O_{46}$ where $A = Pb^{2+}$, Ba^{2+}, La^{2+}, Sr^{2+}. We mostly get these X-type phases blended with phases of M-type and W-type, and it is quite tough to split them [9].

U-type hexagonal ferrites—The chemical composition for such compounds is $A_4Me_2Fe_{36}O_{60}$ where $A = Ba^{2+}$, Sr^{2+}, La^{2+}, Pb^{2+}. One Y-block and two M-blocks along the c-axis are superimposed for this structure. They have complex structure that is why they are hard to produce. They are beneficial in millimeter wave applications [9].

Barium hexaferrite is one of the chemically stable hexagonal structures acquiring admirable corrosion resistance. Barium ferrites are long-lasting magnet material which are formed on the basis of iron oxide (Fe_2O_3) and barium carbonate ($BaCO_3$). They have very low electrical conductivity, high Curie temperature and moderate permittivity. Barium hexaferrites are also chemically compatible with biological tissues; hence, they have a lot of importance in biomedical applications [11]. They have high microwave magnetic loss. There are different methods to produce barium ferrites such as hydrothermal, sol–gel combustion, spray pyrolysis, citrate precursor, co-precipitation and ball milling. Barium ferrites having morphology like platelet are considered best microwave absorbing material [8].

The plethora of dopants were used to alter the properties of barium hexaferrites. But the substitution of rare earth dopants such as dysprosium (Dy), terbium (Tb), erbium (Er), europium (Eu), holmium (Ho), etc., had tailored the properties of ferrites in a very appreciable manner. Rare earth elements were first spotted in the 1960s. They have illustrative hold on structural and magnetic properties of barium ferrites. These rare earth elements can be used widely in intensifying the coercive field and magnetization [12, 13]. They can also work as inhibition agent in mechanism of grain growth at high temperature. The analysis of the electrical resistivity and dielectric consequences on addition of doping of rare earth elements unfolds relevant data regarding the functioning of free electrical and localized charge bearers which gives us better understanding of the mechanism of electrical conduction.

2 Literature Review

2.1 *Wang Jing et al. (2006)*

Dysprosium (Dy), neodymium (Nd) and praseodymium (Pr) were switched in the sample of W-type barium ferrites of composition $Ba(MnZn)_{0.3}Co_{1.4}R_{0.01}Fe_{15.99}O_{27}$. This whole procedure was done using chemical co-precipitation method. After examination, it was clear that the Fe^{3+} could be replaced by some RE^{3+} and modify the hyperfine variables. The loss in reflection and matching thickness of single-layered ferrite absorber was measured. There was a keen decrease in complex permittivity, and in addition to this, high-frequency relaxation and natural resonance frequency were increased. If the ferrite material is substituted with the rare earth element, dysprosium, then it gives out remarkable microwave absorption effects. At the value of 2.1 nm, the matching thickness value reaches up to −51.92 dB. The bandwidth touches the value greater than 8.16 GHz, and frequency starts with 9.9 GHz [14].

2.2 *M. A. Ahmed et al. (2007)*

A configuration of W-type barium hexagonal ferrite was prepared with composition of $Ba_{0.95}R_{0.05}Mg_{0.5}Zn_{0.5}CoFe_{16}O_{27}$ substituted with rare earth ions like Y, Er, Ho, Sm, Nd, Gd and Ce. This was done by double sintering ceramic process. X-ray diffraction specimens were used to characterize the structural properties of the sample and proved the existence of secondary phase. On increasing the ionic radius of rare earth ions, the strength of secondary phase also increases. The value of curie temperature also increases with the increase in concentration of rare earth ions samarium up to 1.04 angstrom and after that it starts decreasing after touching the maximum value. Faraday's method was implemented to study the discrepancy in magnetic susceptibility in temperature range 300–750 K at various amounts of magnetic field applied (1280, 1733, 2160 Oe) [12].

2.3 *Aria Yang et al. (2007)*

M-type hexagonal ferrite ($BaFe_{12-X}Sc_XO_{19}$) was made by substituting scandium. The method for this preparation was conventional ceramic technique. The values for anisotropy and magnetization both reduced on addition of scandium. It was concluded that bipyramidal sites were strongly preferred by scandium addition. Microwave and DC effects were studied extensively in this research [15].

2.4 M. A. Ahmed et al. (2009)

The effect of various rare earth dopants in the form of R_2O_3 where R = Y^{3+}, Er^{3+}, Ho^{3+}, Sm^{3+}, Nd^{3+}, Gd^{3+} and Ce^{3+} ions in chemical composition $Ba_{0.95}R_{0.05}$ $Mg_{0.5}$ $Zn_{0.5}$ Co Fe_{16} O_{27} on electrical properties of W-type hexaferrite had been investigated. The results concluded that on introduction of R_2O_3 alteration of both physical and structural properties can be achieved. Samarium (Sm^{3+}) has highest values of dielectric constant (ε') and dielectric loss factor (ε") and AC conductivity, but these factors decrease with increase in frequency. Semiconducting properties were indicated for these samples where AC conductivity increases with increase in temperature. Majority charge carriers were found to be electrons except in the case of Er^{3+} and Y^{3+} ions. Increase of charge carrier's concentration (n) was there with the substitution of Ba^{2+} ions by R^{3+} ions [16].

2.5 Ji-Jing Xu et al. (2009)

By using sol–gel method, Z-type ferrites doped with La^{3+} with composition $Ba_{3x}La_xCo_2Fe_{24}O_{41}$ (x ¼ 0.00–0.30) were synthesized. And the influence of La^{3+} being a rare earth dopant on the different properties' composition was being characterized. The result of magnetic data resulted that increasing the concentration on La^{3+} ions from 0.0 to 0.3 makes the ferrite a better soft magnetic material. It is because of increase of magnetization and decrease of coercivity [17].

2.6 Huang Xiaogu et al. (2010)

By polymer adsorbent combustion method, W-type barium ferrites having chemical composition $Ba_{1-x}Er_x(Zn_{0.3}Co_{0.7})_2Fe_{16}O_{27}$ ($x = 0.00, 0.05, 0.10, 0.15, 0.20$) were synthesized by substituting Er^{3+}. X-ray diffraction analysis (XRD), X-ray fluorescence (XRF) and scanning electron microscopy (SEM) were done to characterize the crystal structure, surface morphology and electromagnetic properties. On doping content of 0.10 Er^{3+} ions, electromagnetic properties were quite improved [18].

2.7 Imran Khan et al. (2011)

By using simple chemical co-precipitation method, W-type strontium hexagonal ferrites having chemical composition $Sr_{1-x}Ce_xCo_2Mn_yFe_{16-y}O_{27}$ ($x = 0.00, 0.02, 0.04, 0.06$ and $y = 0.0, 0.2, 0.4, 0.6$) have been synthesized. The influence of rare earth dopant Ce at Sr and Mn at Fe site on the structural, magnetic and electrical properties had been characterized. Different properties such as saturation magnetization, remanence, squareness ratio and coercivity were observed using hysteresis loop concluding at room temperature resistivity decreases with increasing content of Ce^{3+} and Mn^{2+} ions. It can be due to the fact that the substitution of Ce^{3+} at Sr^{2+} site increases the concentration of Fe^{2+} ions at octahedral site. There is increase in saturation magnetization and remanence and coercivity with Ce–Mn ion concentration. Hence, it can be used in high-density recording media [19].

2.8 *Faiza Aen et al. (2011)*

W-type hexagonal ferrites having a composition of $BaHo_xFe_{16-x}O_{27}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) were conducted using co-precipitation technique at high temperature of 1320 °C. Single phase of ferrites was observed by XRD. On substituting the amount of Ho, magnetization increases. It is due to the difference in ionic radii of Ho^{3+}, that is, 0.901 A°, and Fe^{3+}, that is, 0.67 A°. Because of separation between grains, it was observed that DC resistivity increases on increasing concentration of Ho^{3+} at room temperature. And DC electrical resistivity works as a function of temperature; it expresses the semiconducting behavior [20].

2.9 *Fengying Guo et al. (2012)*

W-type hexaferrites, $Ba_{0.9}RE_{0.1}Co_2Fe_{16}O_{27}$ sample, were made with the substitution of rare earth ions (La^{3+} , Nd^{3+} , Sm^{3+}). The method used for this preparation was solid-state reaction method at the temperature of 1250 °C for time period of 5 h. X-ray diffraction and scanning electron microscopy technique were used to explore the microstructure. As an outcome, single phase of W-type barium ferrite emerged as platelet-type shape. There was a gradual decrease in lattice parameter ‘a’ and ‘c’ with the decrease in the ionic radius of rare earth dopant. Vector network analyzer counted the complex permittivity and complex permeability from the scale of 0.5–18.0 GHz. Also, the microwave absorbing properties of the sample were highly increased in super-high frequency. Highest value of the dielectric loss tangent angle (0.75) at 16 Hz frequency was given by La-doped ferrite [8].

2.10 *Irshad Ali et al. (2013)*

Nanostructure Tb–Mn-substituted Y-type hexaferrites having single phase with chemical formula $Sr_2Co_{2x}Mn_xTb_yFe12_yO_{22}$ ($x = 0.0–1$, $Y = 0.0–0.1$) were prepared using micro-emulsion method. Polaron hopping is the conduction mechanism in the ferrite system as the content of Tb–Mn increases the DC electrical conductivity. The samples which are having high conductivity have low activation energy. Maxwell–Wagner model and Koop's phenomenological theory were used to explain the frequency-dependent AC conductivity. High value of quality factor is obtained, and Tb–Mn substitution helps to alter and improve electric and dielectric properties [21].

2.11 S. Cai et al. (2013)

Various rare earth elements such as lanthanum (La), dysprosium (Dy), neodymium (Nd), praseodymium (Pr), samarium (Sm), gadolinium (Gd) and ytterbium (Yb) M = Zn^{2+}, Mn^{2+}, $Mn^{2+}_{0.5}$, $Zn^{2+}_{0.5}$ were doped in the composition of M-type barium hexaferrite powders ($Ba_{0.95}Re_{0.05}Fe_{12}O_{19}$ and $Ba_{0.95}Re_{0.05}M_{0.05}Fe_{12}O_{19}$) with sol–gel self-combustion method. X-ray diffraction (XRD) and vibrating sample magnetometer (VSM) techniques were helpful for determining the structural composition of phase sample and magnetic effects. The average diameter of the magnetoplumbite of the sample was known to be 45 nm. Magnetic saturation was not altered by magnetic moments of rare earth ions. On decreasing the concentration of rare earth ions, there was also decrease in saturation magnetization except the Sm^{3+} and Gd^{3+}. Also based on anisotropy, when orbital quantum numbers for ions except Sm^{3+} and Gd^{3+} increased, H_C firstly increased and then decreased [22].

2.12 Irshad Ali (2014)

Y-type hexagonal ferrites with composition of $Ba_2Zn_2Tb_xFe_{12x}O_{22}$ (0 6 × 6 0.1) were prepared using sol–gel auto-combustion method. Maxwell–Wagner type of interfacial polarization and the exchanging of charge carrier between Fe^{2+} and Fe^{3+} ions result in the dispersion of dielectric constant and dielectric loss at low temperature. The dielectric permittivity decreases with Tb^{3+} ion addition. The DC resistivity increased from 7.29×10^7 to 4.73×10^8 ohm cm because of unavailability of Fe^{3+} ions at octahedral sites. These properties are suitable for fabricating multi-layer chip inductors (MLCls) with low eddy current losses and surface effect of materials [23].

2.13 Shihai Guo et al. (2014)

X-ray diffractometer and scanning electron microscopy were used to characterize the Sm^{3+}-doped Co Z-type hexagonal ferrite structures which were prepared by conventional ceramic method. After that, the effect on magnetic and different properties on that composition was observed on addition of Sm^{3+} ions. The hysteresis loop expressed that the saturation magnetization for Sm^{3+} doped was more than that of undoped. After sintering at temperature of 1250 °C, samarium-doped Co Z-Type hexagonal ferrites show good high-frequency properties [24].

2.14 Ali Sharbati et al. (2015)

W-type of hexagonal ferrite with composition of $BaNi_2Dy_xFe_{16-x}O_{27}$ ($x = 0$–0.9) was examined with the substitution of dysprosium. Citrate precursor method was preferably used during the preparation of the sample. Different properties like morphology, DC resistivity, crystalline structure and magnetic properties were investigated by using various techniques like X-ray diffraction (XRD), transmission electron microscopy (TEM), vibrating sample magnetometer (VSM) and vector network analyzer (VSA). The sample was kept heated at the temperature of 1250 °C for 4 h in the air. The hysteresis loop traced provided the increasing values of coercivity with addition of dysprosium (530–560 Oe). The saturation magnetization was decreasing on increasing the content of dysprosium and other magnetic effects. But DC resistivity took its value from 0.83×10^7 to 6.92×10^7 cm with increasing value of the dopant. The reason for this was that there were no Fe^{3+} ions present. Microwave properties of the sample reside between the range of 12 and 20 GHz. Minimum reflection loss (40 dB) was noticed at 16.2 GHz at $x = 0.6$ for 1.7-mm-thick layer [25].

2.15 Javed Rehman et al. (2016)

Single-phase terbium (Tb)-doped X-type hexagonal nano-ferrites having chemical composition $Sr_2NiCoTb_xFe_{28x}O_{46}$ (x ¼0.00, 0.05, 0.1, 0.15, 0.2) were synthesized with micro-emulsion method. Hexaferrites were confirmed by the spectral bands. The dielectric constant was found to be 12.5 at low frequency, while it decreased to 6.5 at high frequency. Introducing terbium reduced the saturation magnetization from 76 to 54 emu/g. Remanence was lowered from 27 to 21 emu/g. On increasing terbium, the coercivity was increased from 610 to 747 Oe [26].

2.16 Muhammad Irfan et al. (2016)

A composition of strontium hexaferrite as $Sr_2MnNiFe_{12}0_{22} + xY_2O_3$ ($x = 0$–5 wt.%) was synthesized and proceeded with different processes like X-ray diffraction (XRD), scanning electron microscopy (SEM) and dielectric spectroscopy for observation. Doping of yttrium reduced the growth of grain. Low saturation magnetization and high coercivity were indicated after yttrium doping to hexaferrites which are quite good magnetic properties [27].

2.17 Kush Rana et al. (2016)

Barium and cobalt used hexagonal ferrite with configuration of $BaCo_{0.8}Sm_XFe_{(11.2-X)}O_{19}$ where $X = 0.2, 0.4$ and 0.6 with substitution of samarium was produced with the help of citrate precursor technique. Various characterization methods were implemented to look over the sample. Emergence of M phase with average crystalline proportions of 35–45 nm was examined by XRD. Transmission electron microscopy and field emission scanning electron microscopy were also drawn for the material sample. During vibrating sample magnetometer (VSM), field of 22,000 Oe was put in at the room temperature and then B–H loops were traced. It was noticed that as samarium ions are increased, there is decrease in retentivity, coercivity and specific saturation magnetization. The best values for coercivity and squareness ratio were found at the 0.2 value of x. These values are 2690.20 Oe and 0.5619, respectively [5].

2.18 Maria Zahid et al. (2017)

Y-type hexaferrites with chemical composition $Ba_2NiCoDy_xFe_{12\text{-}x}O_{22}$ ($x = 0.00$, 0.05, 0.01, 0.15, 0.20, 0.25) were synthesized using sol–gel auto-combustion method. As frequency is increased, there is a decrease in electrical permittivity. It can be due to interfacial polarization which can be described with the help of Maxwell–Wagner model. Magnetization decreases because of segregation of Dy at grain boundaries. And coercivity also decreases on increasing the content of Dy due to exchange coupling effect between neighboring domains [3].

2.19 Anum Zafar (2017)

Magnetic and electrical properties of M-type barium hexaferrites were discovered. The sample was prepared by hydrothermal technique with substitution of Euat 0, 0.02, 0.04, 0.08 and 0.10. The single phase of M-type hexagonal structure was proved by the XRD and FTIR which was done at the range of 40–100 MHz. The increased conductive behavior was shown by dielectric constant at low frequency. There was an increase in saturation magnetization from 30.49 to 54.27 emu/g and in coercivity 3.03–8.73 KOe with doping of the Eu [28].

2.20 *Vipul Sharma et al. (2018)*

M-type hexagonal barium ferrite is a kind of magnetic material which gives a lot of information about electromagnetic wave propagation in different microwave devices. They have large magnetization. Ferromagnetic resonance study of rare earth elements such as neodymium (Nd) and samarium (Sm), taking cobalt (Co) as base, doped hexaferrite nanoparticles. Different techniques such as X-ray diffraction, vibrating sample magnetometer (VSM) and ferromagnetic resonance (FMR) were used to check the structure and magnetic properties of doped hexaferrite nanoparticles. Substituting different rare elements like Nd and Sm has a great effect on electromagnetic properties of hexaferrites. Hydrothermal method is one of the best method for the synthesis of rare earth (Nd and Sm) doped M-type hexaferrites. Magnetization saturation was going down from 73.2 emu/g for (S1) pure BaM to 45.4 emu/g for $S_3(BaCo_{0.5}Nd_{0.3}Fe_{11.})$. The doped samples showed resonance behavior lesser than the pure phase from 16 to 30 GHz [11].

2.21 *Muhammad Faisal et al. (2018)*

Different compositions of nano-crystalline M-type barium hexagonal ferrites with cobalt–samarium doping $BaFe_{12-2Z}Co_ZSm_ZO_{19}$ were analyzed at ($Z = 0.0, 0.2, 0.4, 0.6$). This sample was prepared with WOWS sol–gel method without using water and surfactants. XRD patterns were examined to give out lattice constant, crystal size, porosity and theoretical density. LCR meter surveyed the dielectric specifications. Material morphology was discovered by scanning electron microscopy. Temperature was set up to 100–400 °C to verify the DC electrical resistivity. Large values of Curie temperature, magnetization, magneto-crystalline anisotropy and dielectric effects were unfolded. XRD concluded the hexagonal structure. The size of sample material was spilled about 295 nm to 440 nm by SEM. The ferromagnetic effect was elucidated at 25 °C by the hysteresis loop. The nano-crystalline structure was confirmed by the coercivity displayed by Sm^{3+} and Co^{2+} ions [7].

2.22 *Safia Anjum et al. (2019)*

$Ba_{1-x}La_xFe_{12}O_{19}$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$) which is a M-type barium hexaferrite was prepared through conventional ceramic route to know the effect of La^{3+} ions on various properties like structural, dielectric, optical and magnetic properties. Hexagonal structure of La^{3+}-doped Ba hexaferrites was confirmed by XRD. Stretching vibration of oxygen and metal (Fe–O) might be resulted that the bands are in the range 500–600 cm^{-1} confirmed by FTIR. Lanthanum substituted in M-type barium hexaferrite confirms the magnetoplumbite structure of La^{3+} ions which was confirmed by XRD and FTIR. With increase in concentration of La^{3+} ions, band gap energy decreases, while the coercivity increases with the La^{3+} ion substitution because of ordering of paramagnetic La^{3+} at A-site which suppresses the ferromagnetic order. On increasing amount of lanthanum in M-type barium hexaferrite, the tangent loss decreases and AC conductivity increases at high frequency [6].

2.23 *J. Mohammed et al. (2019)*

Cu^{3+}–Er^{3+}-substituted M-type strontium hexaferrites having chemical formula $Sr_{1\text{-}x}Cu_xFe_{12\text{-}y}Er_yO_{19}$ ($x = 0.0, 0.1, 0.2$, and $y = 0.0, 0.4, 0.5$) were prepared using sol–gel auto-combustion method which was pre-sintered at 300 for 3 h and then after sintered at 1000 for 6 h. XRD gives the sample structure to be pure crystalline with the absence of magnetite (α-Fe_2O_3) and other secondary phases. Band gap increases with the content of Cu^{3+} –Er^{3+} calculated by UV–Vis NIR spectroscopy. Given samples show low dielectric loss with dielectric constant at high frequency. Ferromagnetic behavior was expressed by magnetization loop. Magnetic properties decrease with increase by substituting Cu^{3+}–Er^{3+} [29].

2.24 *İsa Araz (2019)*

$Ba_{0.5}Ce_{0.5}Fe_{11}CoO_{19}$ chemical composition of barium hexaferrite with substitution of Ce–Co was prepared by ceramic technique. Dual phase was characterized by XRD grain size around 66.55 nm. The magnetizations were decreased with increase in Ce^{3+} ions. In the ferrite structure, more addition of Ce^{3+} ions gives rise to the conversion of some Fe^{2+} ions at the tetrahedral site from Fe^{3+} ions at octahedral sites to Fe^{2+} ions at the tetrahedral site. The spectrum of the complex intrinsic parameters and the electromagnetic wave absorbing was of range in between 2.0 and 18.0 GHz frequency range. Ce substitution to the barium hexaferrite was quite helpful in improving the electromagnetic wave absorbing ability. It can be considered quite efficient material for shielding and absorption application in microwave field [30].

2.25 *Mohammad K. Dmour et al. (2019)*

Using the famous preparation method of sol–gel, a complex configuration $Ba_{1-x}Re_xCo_2Zn_xFe_{16-x}O_{27}$ was made and the few rare elements containing lanthanum (La), neodymium (Nd) and praseodymium (Pr) were mixed in the composition as ($x = 0.0, 0.1, 0.2$). It was then sintered at the temperature of 1250 °C for near about 2 h. Electromagnetic and microstructural effects were perceived. XRD technique gave the traces for pure W-type hexaferrite phase for all samples leaving neodymium–zinc at $x = 0.2$ that was mixed with M-type phase in addition to W-type. Beneath the temperature of 300 °C, spin reorientation transformation was disclosed by the thermomagnetic curves. Magnetic transition was on the scale of 461–481 °C. It was also divulged that as RE–Zn concentration is made higher, there is a gradual increase in magneto-crystalline anisotropy field. This increase was given as (6.30–9.23 KOe). At the temperature values of 505–516 °C, weak magnetic phase transitions were revealed with cobalt-rich impurity magnetic phase [31].

The observed values of structural and magnetic parameters obtained from the literature review are summarized in Tables 1 and 2.

Transformation of abundant barium hexaferrites treated with rare earth elements like dysprosium, terbium, erbium, holmium, samarium and many others was registered down. Change in magnetic properties was noted with altering values of saturation magnetization, retentivity and coercivity. Semiconducting properties changed with growth in AC conductivity on increasing temperature. Elements like lanthanum, neodymium and samarium increased the magnetization saturation, retentivity and coercivity values influencing the magnetic properties. In some of the compositions, addition of cerium decreased the values of magnetization saturation, retentivity and coercivity. But on the average, net enhancement in electromagnetic properties of rare earth doped hexaferrites has been observed which increase their utility in high-frequency operating devices.

3 Synthesis Techniques Used to Prepare the Rare Earth-Doped Samples

Rare earth-doped hexaferrites can be prepared using various synthesis methods as shown in Fig. 4.

3.1 Sol–gel

This process emerged in the year 1921. It is a chemical method for preparing ceramic powders, gels and glasses. During this process, gels can be broken into granules when they are in the drying state. The materials required in this process are of inorganic configuration having various properties like superconductivity and ferroelectricity. It comprises various steps like solution, gelation, drying and densification. Firstly, a silicate solution is prepared in this process and then gel formation takes place. A sol is prepared with dispersion of colloidal particles (crystalline and amorphous). After this, a dry gel is obtained which is made up of 3-D network of silica. In this drying process, remaining solvent is removed. And after that final sintering, densification and grain growth mechanism are done to enhance the mechanical properties and the stability of the structure. Refer Fig. 5 for stepwise procedure of sol–gel method.

Table 1 Observed values of structural parameters

Composition	a (Å)	c (Å)	c/a (Å)	Reference no.
$Ba(MnZn)_{0.3}Co_{1.4}RE_{0.01}Fe_{15.99}O_{27}$ (RE = Dy^{3+}, Nd^{3+},Pr^{3+}	5.90719–5.9028	32.92385–32.92554	–	[14]
$BaCo_2La_xFe_{24}O_{41}$ ($x = 0.0$–0.3)	5.883–5.96	5.2311–5.2548	8.892–8.852	[17]
$Sr_{1-x}Ce_xCo_2Mn_yFe_{16-y}O_{27}$ ($x = 0.0$–0.06, $y = 0.0$–0.6)	5.83–5.89	33.30–33.94	–	[19]
$BaHo_xFe_{16-x}O_{27}$ ($x = 0.0 = 1.0$)	5.86–5.91	32.6–33.45	5.55–5.66	[20]
$Ba_{0.9}RE_{0.1}Co_2Fe_{16}\_O_{27}$ (RE = La^{3+}, Nd^{3+}, Sm^{3+})	5.896 ± 0.0011–5.889 ± 0.0013	32.025 ± 0.0001–32.805 ± 0.0002	–	[8]
$Ba_2Zn_2Tb_xFe_{12-x}O_{22}$ ($x = 0.00$–0.10)	5.85–5.91	43.45–44.31	7.41–7.49	[23]
$BaNi_2Dy_xFe_{16-x}O_{27}$ ($x = 0$–0.9)	0.5866–0.5877	3.3261–3.3273	5.670–5.661	[25]
$Sr_2NiCoTb_xFe_{28-x}O_{46}$ ($x = 0.00$–0.2)	5.283–5.282	83.720–83.726	15.847–15.851	[26]
$Ba_2NiCoDy_xFe_{12-x}O_{22}$ ($x = 0.00$–0.25)	5.87–5.88	43.87–43.97	7.47–7.48	[3]
$BaFe_{12-2x}Co_xSm_xO_{19}$ ($x = 0.0$–0.6)	5.883 ± 0.500–5.864 ± 0.500	23.037 ± 0.500–22.998 ± 0.500	3.915–3.922	[7]
$La_xBa_{(1-x)}Fe_{12}O_{19}$ ($x = 0.0$–0.5)	5.8609–5.8655	23.0239–22.8198	3.92–3.88	[6]
$Sr_{(1-x)}Cu_xFe_{12-y}Er_yO_{19}$ ($x = 0.0$–0.2, $y = 0.0$–0.5)	5.91–5.87	23.27–23.15	3.937–3.943	[29]

(continued)

Table 1 (continued)

Composition	a (Å)	c (Å)	c/a (Å)	Reference no.
$BaCe_xFe_{11}CoO_{19}$ ($x = 0$–0.5)	5.893–5.892	23.185–23.183	3.9343–3.9356	[30]
$Ba_{(1-x)}RE_xCo_2Zn_xFe_{16-x}O_{27}$ ($x = 0.0$–0.2)	5.90–5.89	32.89–32.83	–	[31]

Table 2 Observed values of magnetic parameters

Composition	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	Reference no.
$Ba_{3-x}Co_2La_xFe_{24}O_{41}$ ($x = 0.0$–0.3)	61.36–77.31	5.682–5.556	45.68–35.51	[17]
$BaHo_xFe_{16-x}O_{27}$ ($x = 0.0 = 1.0$)	3.648–31.831	1.334–14.492	1041.7–1709.6	[20]
$Ba_{0.9}RE_{0.1}Co_2Fe_{16}\_O_{27}$ ($RE = La^{3+}$, Nd^{3+}, Sm^{3+})	82.06–82.70	10.02–11.63	747.0–854.3	[8]
$BaNi_2Dy_xFe_{16-x}O_{27}$ ($x = 0$–0.9)	74–53	–	530–560	[25]
$Sr_2NiCoTb_xFe_{28-x}O_{46}$ ($x = 0.00$–0.2)	76–54	27–21	610–747	[26]
$BaCo_{0.8}Sm_xFe_{11.2-x}O_{19}$ ($x = 0.2$–0.6)	32.55–21.36	18.25–10.65	2690.20–2407.52	[5]
$Eu_xBa_{1-x}Fe_{12}O_{19}$ ($x = 0$–0.10)	30.49–54.27	–	3030–8730	[28]
$BaCo_xFe_{12}O_{19}$ ($x = 0$–0.5)	77–63.3	–	5200–2360	[11]
$BaFe_{12-2x}Co_xSm_xO_{19}$ ($x = 0.0$–0.6)	62 ± 0.5–61 ± 0.5	40 ± 0.5–35 ± 0.5	5267 ± 10–3087 ± 10	[7]
$La_xBa_{(1-x)}Fe_{12}O_{19}$ ($x = 0.0$–0.5)	–	2.085–1.515	409.08–590.18	[6]
$Sr_{(1-x)}Cu_xFe_{12-y}Er_yO_{19}$ ($x = 0.0$–0.2, $y = 0.0$–0.5)	59.41–51.84	34.07–29.27	6031.74–4962.09	[29]

(continued)

Table 2 (continued)

Composition	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	Reference no.
$BaCe_xFe_{11}CoO_{19}$ ($x = 0$–0.5)	60–42.4	26.42–12.5	1159–462	[30]
$Ba_{(1-x)}RE_xCo_2Zn_xFe_{16-x}O_{27}$ ($x = 0.0$–0.2)	73.03 ± 0.09–74.60 ± 0.08	11.42 ± 0.50–6.26 ± 0.60	95 ± 5–80 ± 5	[31]

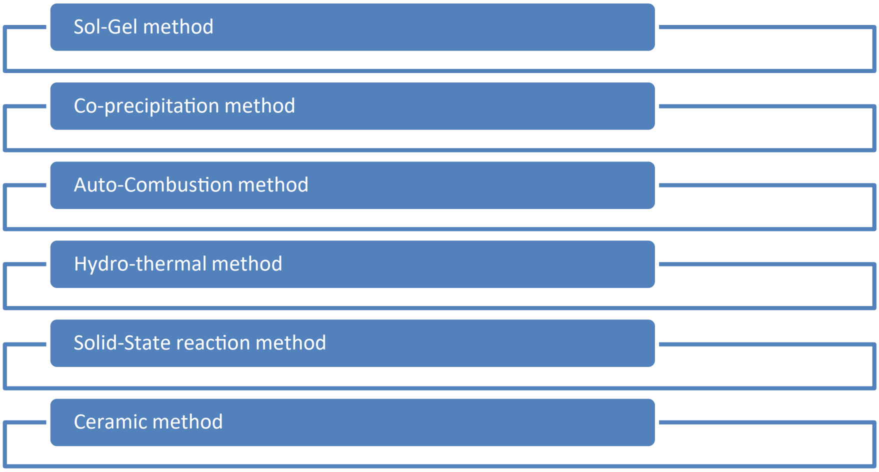
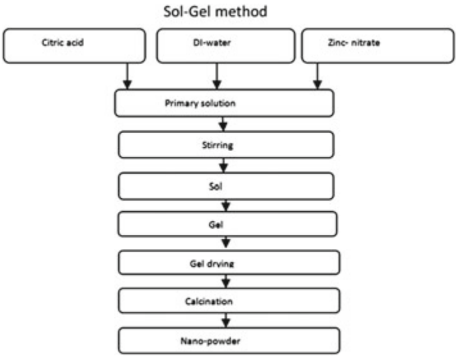


Fig. 4 Different synthesis techniques for preparing rare earth-doped samples

Fig. 5 Sol–gel method



3.2 Co-precipitation

It is a method in which a solute is precipitated out by some of the forces but normally that solute remains dissolved in the solution. This is facilitated by some of the chemical reaction made in the laboratories. The imperative forces pull out the solute from the dispersed medium. In this method, magnetic stirring at the temperature of 70 °C is done; after that in centrifugation process, particles are cleared by the deionized water, and in the last step, the resulted part is dried. In Fig. 6, various steps involved in the process of co-precipitation method are shown.

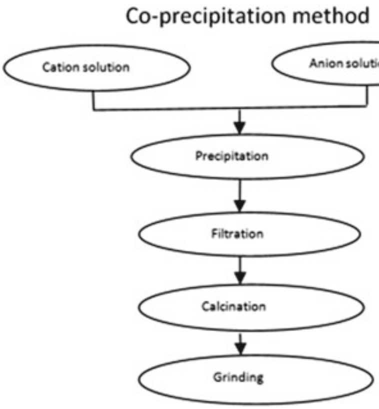


Fig. 6 Co-precipitation method

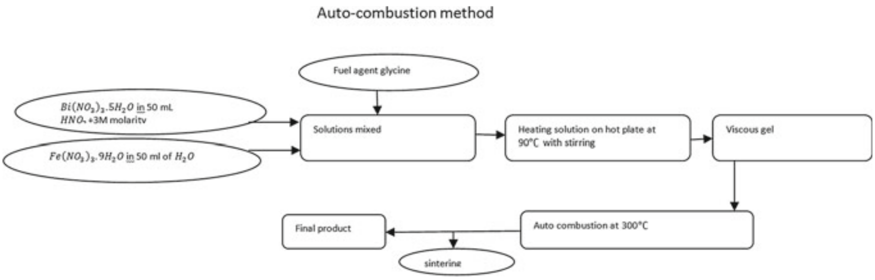


Fig. 7 Auto-combustion method

3.3 Auto-combustion Method

In this method, the solution of ammonia, citric acid and salts is set up to pH value of 7, and then on a dry plate, they are evaporated. Carbon dioxide gas is given out when polymerization of the citric acid takes place. Cations are changed into the barium carbonate and oxides of iron. Small grain-sized sample is obtained which is in last auto-combusted in the microwave oven to get the nano-powder. Auto-combustion method is described in Fig. 7.

3.4 Hydrothermal Method

It is a process in which single crystals (nanoparticles) are synthesized depending on the solubility of the minerals in the hot water. Crystal growth is taken out in a steel vessel called autoclave at high pressure. Temperature is kept constant in this process.

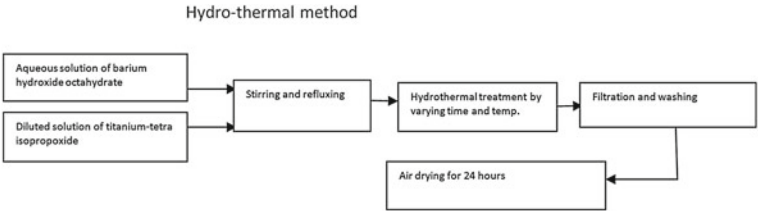


Fig. 8 Hydrothermal method

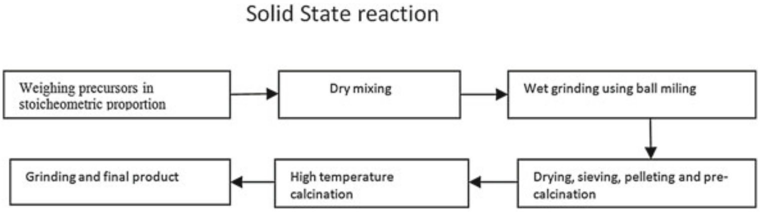


Fig. 9 Solid-state reaction

It is an effective method for preparing those crystalline phases which are not so much stable at higher temperature. Figure 8 shows the process of hydrothermal method.

3.5 *Solid-State Reaction Method*

As shown in Fig. 9, it is the simplest method for producing the single crystals and polycrystalline powders of phosphates and arsenates of transition metals and monovalent cations. In this process, required amount of precursors is taken and then they are grinded. The resulted powder is then heated at 350–400 °C resulting in the removal of ammonia, carbon dioxide, water and other nonvolatile substances. After that, grain size is decreased. Cation migration is then done at the high temperature, and then, crystals are separated by boiling water.

3.6 *Ceramic Method*

In this method, barium oxides and carbonate powders are heated to get the hexagonal ferrites. Because of low reactivity of the starters, high temperature is required in this process. Extrusion, slip casting, pressing, tape casting and injection molding are some of the most common ceramic forming methods. Figure 10 shows how the ceramic method is used to prepare the rare earth-doped barium hexaferrites.

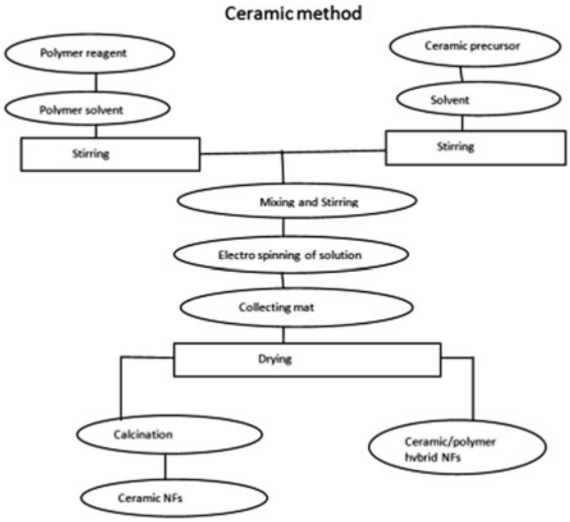


Fig. 10 Ceramic method

4 Conclusion

This paper lays out the detailed data about the verified upgrowth of the barium hexaferrites introduced with rare earth elements. Different types of ferromagnetic oxides with their application areas are discussed. According to the Literature review, the rare earth doped barium ferrites best supports for the enlightenment of electromagnetic properties. Various operating procedures including X-ray diffraction, scanning electron microscopy, etc., provided the useful information about the composition, crystallographic structure, surface topography of the sample, its chemical properties and much more. For various M-type barium hexaferrites, lanthanum ions increase the coercivity and AC conductivity at high frequency. Elements like cerium were used to improve the ability of the sample for absorbing electromagnetic waves. In few of the Y-type barium hexaferrites, DC electrical conductivity grows on addition of terbium like rare earth element. But for strontium hexaferrites, addition of terbium reduced the saturation magnetization and made an increase in coercivity. Samarium, holmium and erbium showed the best high-frequency dielectric properties which made them quite useful for application areas like semiconducting and other high-frequency operating devices. Magnetic properties talk about the most increase in magnetic saturation and coercivity that helps them being useful in field of recording media as permanent magnets, multilayered inductors and chips, etc.

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