RESEARCH ARTICLE

SAMRIDDHI Volume 13, Special Issue 2, 2021 Print ISSN : 2229-7111 Online ISSN : 2454-5767

A Review: Effect of Substitution on Morphological and Magnetic behavior of W-type Hexagonal Ferrites

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ABSTRACT

Hexaferrites have various applications in data storage and magnetic recording materials and in components in electrical devices, especially those operating at microwave/GHz frequencies. These compounds give appealing magnetic characteristics at less cost. Doping of divalent, trivalent and tetravalent ions into the hexagonal ferrite structure enhances the electromagnetic effects. Doping changes the electric and magnetic properties and magnetocrystalline anisotropic fields. In this review, we will explore the modifications in W-type ferrite in terms of magnetic properties, morphology, crystal structure, microwave absorption properties and reflection loss with substitution of different suitable and appropriate magnetic or non- magnetic divalent or trivalent ions into the lattice.

Keywords: W-Type Hexagonal Ferrite, Microwave Absorbing Materials, Reflection Loss, Magnetic Properties, Magnetocrystalline anisotropy.

SAMRIDDHI : A Journal of Physical Sciences, Engineering and Technology, (2021); DOI : 10.18090/samriddhi.v13spli02.32

INTRODUCTION

Ferrites are ceramic compounds which are ferrimagnetic in nature and are composed of iron oxides namely magnetite (Fe_3O_4) as well as oxides of other metals. The structural compounds called as the Spinels contain Magnetite (Fe_3O_4).The composition of cubic structured Spinels are $MeFe_2O_4$, where Me is a divalent cation. Another class of ferrites is named as hexaferrites having hexagonal structure, including lattice parameters 'a' and 'c' which reflect width and height of the crystal respectively. The lattice parameters of the conventional lattice of a hexagonal structure ideally are: a=b and c=1.633a. The crystalline structure of hexagonal ferrites decides their properties. Due to magnetocrystalline anisotropy there are two groups of hexaferrites, one with easy axis of magnetization and other with easy plane of magnetization.[1] Hexagonal ferrites are also known as Hexaferrites, have various applications in data storage and magnetic recording materials and in components in electrical devices, especially those operating at microwave/GHz frequencies. [1,2] Hexagonal composites and their oxides can be used for microwave absorption and permanent magnets due to their instrinsic magnetocrystalline anisotropy and magnetic properties. These compounds give appealing magnetic characteristics at less cost.[3] Due to very prominent magnetocrystalline anisotropy field these compounds exhibit high ferromagnetic resonance in GHz frequency range and they have easy axis of magnetization and easy plane of magnetization. Hexagonal ferrites can be classified into M-, Y-, W-, X-, Z-, and U-type phase based on their chemical composition. Table 1 shows the types

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How to cite this article : Tolani, S.C., Rewatkar, K.G. (2021). A Review: Effect of Substitution on Morphological and Magnetic behavior of W-type Hexagonal Ferrites. *SAMRIDDHI : A Journal of Physical Sciences, Engineering and Technology,* Volume 13, Special Issue (2), 308-319.

Source of support : Nil

Conflict of interest : None

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of hexaferrites with their hexagonal blocks and Molecular formula with units. Out of all the types, M-type hexagonal ferrite has been explored the most for research and electromagnetic absorption applications[4-8].Hexagonal ferrite find various applications especially in the field of microwave wave absorbers in antennas because of their magnetic and prominent dielectric properties. It has been observed that Calcium hexagonal ferrites improve the values of coercivity and grain growth with good control could be achieved.[9]

Table-1: Types of hexagonal ferrites with their Molecular formula, Molecular units and structural blocks. *= 180^0 rotation of that block around the c-axis.

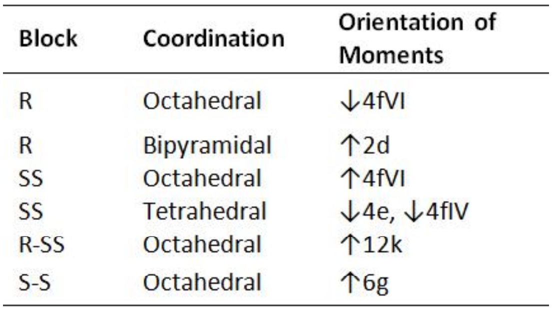
Ferrite	Molecular formula	Molecular units	Hexaferrite blocks
S	$CoFe_2O_4$	S	1/2 S
M	$BaFe_{12}O_{19}$	M	SR
W	$BaCo_2Fe_{16}O_{27}$	M+2S	SSR
X	$Ba_2Co_2Fe_{28}O_{46}$	2M+2S	SRS^*S^*R
Y	$Ba_2Co_2Fe_{12}O_{22}$	Y	ST
Z	$Ba_3Co_2Fe_{24}O_{41}$	Y+M	STSR
U	$Ba_4Co_2Fe_{36}O_{60}$	Y+2M	SRS*R*S*T

Doping of divalent, trivalent and tetravalent ions into the hexagonal ferrite structure enhances the electromagnetic effects.[10-11] Doping changes electric and magnetic properties and magnetocrystalline anisotropic fields in ferrites. Appropriate doping concentrations can increase domain rotation and attaches domain wall displacement. Hence with suitable doping in proper concentrations, magnetic losses can be enhanced and variation in the resonance frequency can be achieved. The parameters like permeability, permittivity and saturation magnetization can be varied and modified by substituting divalent or trivalent ions such as Sr, Pb in Planar Hexagonal Ferrite structures. With substitution of non- magnetic substituent, the magnetic properties can be improved. It has been found that W-type hexaferrites have doubly thick spinel blocks as compared to M-type structure. Hence by suitable addition of divalent cations without changing iron concentration, the magnetic properties can be improvised. It has been observed that over doping and high concentrations of substitutions often increases lattice defects and distortions with formations of different phases. The electron scattering with high doping enhances electric resistivity and ohmic losses. Higher doping concentrations are found to weaken microwave absorption. Hence for impedance matching and microwave attenuation, proper doping concentration should be chosen. It is reported that substitution of Co^{2+} or Ba^{2+} by Mn-Zn metal ions improved the microwave absorption properties of $BaCo_2Fe_{16}O_{27}$ in the in the frequency range of 2 - 18 GHz. [12] The substitution of metal ions in place of divalent ions like Co^{2+} or Ba^{2+} increases the magnetic loss.[12] The substitution of divalent cations like Mg, La, Ga, Cr etc in Zn_2W hexaferrite have improved their magnetic properties. [13,14] The study and synthesis of Strontium Zinc W-type hexaferrite doped with Cobalt and Nickel, the material $SrZn_{2-x}Co_{x/2}Ni_{x/2}Fe_{16}O_{27}$ exhibits strong and better magnetization.[15] It has been reported that substitution of divalent ion such as Sr in place of Ba can manipulate the resistivity, permittivity, permeability and saturation magnetization.[16] The transport properties, dielectric and magnetic properties get affected to great extend due to substitution of diamagnetic and paramagnetic cations in place of Fe^{3+} ions in the lattice.[17,18] The substitution of Mg ions in W-type hexaferrite enhances the magnetic properties.[19]The properties of hexagonal ferrites can be modified by substituting rare earth ions like Sm, Y, Ho, La Nd, Er , and Ce. The relaxation properties of Rare-earth elements (RE) alter the electromagnetic properties of W-type ferrites incredibly specially when they are substituted in place of Ba (Sr) or Fe. [20-22] When rare earth ions like La^{3+}, Nd^{3+} and Ce^{3+} ions on trivalent Fe^{3+} site or on bivalent Ba^{2+} ions enhance electric and magnetic properties and also modify the morphology of the materials.[23-24] In W-type hexaferrites, the magnetic properties, morphology, dielectric properties can be manipulated and altered to great extent by a suitable substitution or doping of divalent or trivalent cations, without changing the iron content. In this review, we will explore the modifications in W-type ferrite in terms of magnetic properties, electric properties, morphology, crystal structure, microwave absorption properties and reflection loss with doping and substitution of different magnetic or non- magnetic ions into the lattice.

W-TYPE HEXAGONAL FERRITES

W-type hexaferrite consists of two Spinel S-blocks above and below one R-block with large divalent Ba/Sr/Pb/Ca- ions. These blocks arrange themselves to form repeated structure of RSSR*S*S* along the c-axis.[25] Further, R and S block coincide together along the c –axis where the [0001] axis of R blocks and [111] axis of S blocks appear simultaneously. These blocks consists of different octahedral and tetrahedral sites with sublattices of seven different types cations.[26] Table 2 shows the positions of iron with the magnetic moments of the sites in W-type crystal.[27] The site preferences of ions strongly suggest the dielectric and magnetic characteristics of W-type hexaferrites. The formation of these two sites for divalent ions per formula unit is due to an additional S-block per formula unit in the structure of W-type hexaferrites. One finds mirror planes containing large cations perpendicular to the hexagonal axis in the lattice of W-type hexaferrite.

Table-2: Orientation Moments of different blocks



Block	Coordination	Orientation of Moments
R	Octahedral	↓4fVI
R	Bipyramidal	↑2d
SS	Octahedral	↑4fVI
SS	Tetrahedral	↓4e, ↓4fIV
R-SS	Octahedral	↑12k
S-S	Octahedral	↑6g

W-type hexagonal ferrite has seven different sites where iron ions exist which are 4fvi, 2d, 12k, 6g, 4f, 4fiv, and 4e or five magnetic sites.[28] By substituting suitable divalent and trivalent ions like Cu, La, Mg, Co, Cr at different sites of W-type ferrite the magnetic properties, resistivity, permeability and permittivity can be improvised. The magnetocrystalline anisotropy of W-type hexaferrites is along the easy c-axis and it can be tuned which makes W-type hexaferrites highly sought after compounds for microwave absorption purposes.[29] W-type hexaferrites are found to have reorientations of the spins between easy plane, easy cone and easy axis due to the effect of either magnetic field changes or temperature variations.[30-32] These spin reorientations are of the first order and changes in the chemical compositions can modify the transition temperatures substantially. These properties indicate that W-type ferrites can be explored to be used in magnetic refrigerators at room temperatures. [33] W-type ferrite is chemically unstable.[34] The phase of W-type ferrite is a combination of Spinel and M –type ferrite blocks (M: $BaFe_{12}O_{19}$, S: $Fe^{2+}Fe_2O_4$). Hence, with suitable substitution of divalent and trivalent cations, the ferromagnetic resonance frequency, Curie temperature, magnetic and electric properties can be improvised as per the need. Also, the microwave absorption characteristics also depend on the microstructure of the W-type hexaferrite.[15] However, there is less research on microwave absorption characteristics of W-type hexaferrite as compared to M –type hexaferrite. Moreover, Fe_2^{2+} W type ferrites are not reported to be synthesized by ceramic method as Fe^{2+} gets oxidized to Fe^{3+}.W- type hexaferrite has a complex structure consisting of a superposition of $T(O_4–BaO_3–BaO_3–O_4)$, $R(O_4–BaO_3–O_4)$ and S spinel block($O_4–O_4$) along the hexagonal c-axis such as RSSR*S*S* where * means the corresponding block has been turned 180^0 around the hexagonal axis.[35] The Spinel blocks and tetrahedral sites of W-type hexaferrite is symmetrically equivalent structures unlike Spinel and Magnetoplumbite . As compared to M-type ferrite, the presence of divalent cations in the structure of W-type hexaferrite makes it feasible to alter its magnetic properties by substitution of divalent cations of suitable choice. As per Lotgering, Barium W-type ferrite has higher energy product BHm than Barium M-type material and hence considered as the permanent magnetic material [36]. Also, Barium W-type ferrite has around 15KOe of anisotropy field and the anisotropy field increases with proper substitutions. It has been observed that with proper substitution of divalent cations like zinc and Nickel, W-type ferrites find applications in wireless networks and commercial drones with frequency range of about 5.8 GHz. Also, the observations suggest that W-type ferrites containing Zn has highest saturation magnetization at low temperatures. With substitution of copper it is found that that anaistrophy of W-type ferrites changes from c –axis to basal plane. As a result of this, CoZn can be used to substitute Fe^{3+} to improve the magnetic characteristics of the ferrite in the high frequency range. However, very less study has been done on

Ca-Substituted W-type hexaferrite which can have effect on cation occupation in the ferrite. The electronic configuration of Calcium is the similar to Pb, Sr and Ba and it lies in the same group in the periodic table. Investigating the properties of Ca^{2+} substituted W-type hexaferrite in place of Ba^{2+} ion would be of great interest as a potential magnetic material for future applications. The structural, magnetic properties and doping effect can be studied for potential applications. The synthesis of W-type hexaferrites at the nanoscale reduces thickness of microwave absorber coatings and enhances the absorption efficiency due to nanocrystalline nature.[37] W-type hexaferrites have various applications in electromagnetic wave absorption, permanent magnets, bubble domain memories and magnetic refrigerators because of their strong anisotropy and moderate magnetization.[38] Still, there are fewer publications on the W-hexaferrite so far and hence W-type hexaferrites become the compounds of special focus for potential application and studies. The synthesis of W-type composites with suitable substitutions, different dimensions and appropriate synthesis methods will help pave way in development of functional materials with novel applications.

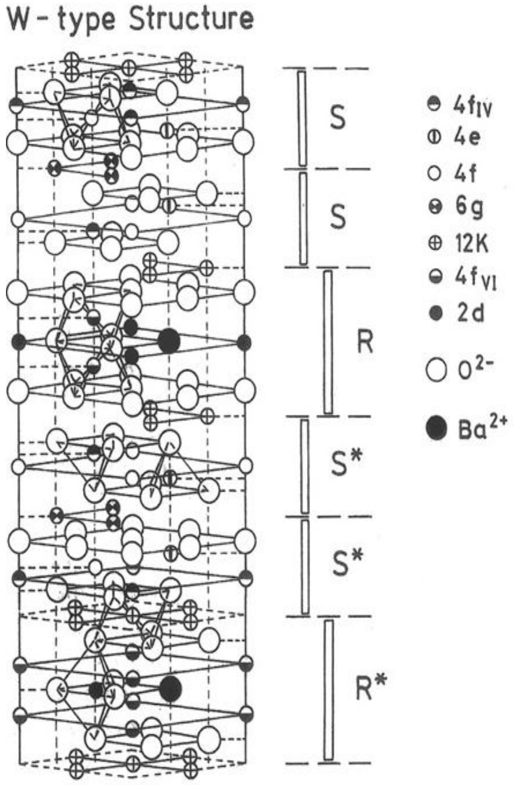


Figure 1: The View of Barium W-type Hexagonal Ferrite. [1]

EFFECT OF SUBSTITUTION ON

Crystal Structure And Anaisotrophy

The ferrite crystal and its structure determine its magnetic properties. W-type hexagonal ferrite is a mesh of positively charged metal ions and negatively charged oxygen ions. The packing of oxygen layers are very close in the structure of W-type hexaferrite. It is observed that the substitution of Zn ions reduces the crystal anisotropy on the basal plane and substitution of Ni ions changes the magnetization from basal plane to c-axis [39]. When rare earth ions like Ce, La, Gd etc are doped in the W-type hexagonal ferrite, it is observed that with increase in the radius of ions, the porosity also increases. This increase continues till increase in rare earth ionic radius goes upto maximum value, and then it reduces. This enhancement in porosity is due to ion radius being less than 1.04 A^0 resulting in ions going into the hexagonal structure. The decrease in porosity after maximum ion radius is due to most ions going out of the hexagonal structure to form a phase on the grain boundaries. Due to replacement of Barium ions in W-type hexaferrite with rare earth ions, lattice constant 'c' reduces with enhacement in the ionic radius of ions. As a result of which the substitution of rare-earth ions in barium hexaferrite shrinks the structure. When W-type $Ba(MnZn)_xCo_{2(1-x)}Fe_{16}O_{27}$ samples are synthesized, through suitable doping of MnZn, the crystal structure with a hexagonal shape and morphology are observed. In $CaSr_2(MnZn)_{x/2}Fe_{16-x}O_{27}$ with (x = 0 to 1) the lattice constant 'a' decreases and lattice constant 'c' values increases with concentration of impurities.[12]This change in lattice parameters arises because of different radius of Mn and Zn ions. The increase in concentration of MnZn increases the densities which decreases the porosity. With Mg content, the lattice parameter (a) decreases and parameter (c) increases in $BaCoZn_{1-x}Mg_xFe_{16}O_{27}$. This variation in lattice parameters is due to occupancy of tetrahedral sites by cations of different radii as a result of doping. The porosity of the composition increases as a consequence of decrease in porosity because Mg^{2+} ions occupy tetrahedral sites partially and octahedral sites more whereas Zn^{2+} ions occupy tetrahedral sites. A reported strontium W-type ferrite $SrZn_{2-x}Co_{x/2}Ni_{x/2}Fe_{16}O_{27}$

reveals less values of lattice constants ‘a’ and ‘c’ by substitution of Co^{2+} and Ni^{2+} instead of Zn^{2+} cations compared to those for pure sample. The reduction in the lattice constants and the distance between lattice planes leads to shrinking in the structure of the strontium W-type hexagonal ferrite. It is observed that introducing MnZn in W-type crystal structure create no change in the structure with different substitution concentration.

Morphology

The surface morphology indicates the creation of ferrite grains in the nano-scale. The SEM study reveals shapes and the particle sizes ranging of the W-type compound. The micrograph helps in identifying crystal formation with compositional homogeneity. It has been observed that La^{3+} doped hexagonal ferrite $Ba_{0.8}La_{0.2}Co_{0.9}Zn_{1.1}Fe_{16}O_{27}$ exhibit planar and hexagonal morphology. It shows a smooth surface and flaky shaped grains. It is found that $BaCoZn_{1-x}Mg_xFe_{16}O_{27}$ the W-type has homogeneous hexagonal crystals with grain size of 3mm and 6 mm due to change in composition.[19] In a cadmium-containing W-type hexagonal ferrite $SrCd_2Fe_{16}O_{27}$ shows a high morphological homogeneity and grain sizes ranging from 0.05-0.075 gm.[40] Using nanocrystalline materials enhances the coercive forces as due to nanoscale the multiple magnetic domains change to single in the structure. Nanocrystalline materials give broader bandwidth of absorption of electromagnetic waves in less thickness of the film. W –type ferrites with hexagonal plate like or pyramidal morphology are being extensively used as radar absorbing materials. In Strontium W-type ferrite $SrZn_{2-x}Co_{x/2}Ni_{x/2}Fe_{16}O_{27}$ with the doping of nickel and cobalt ions instead of zinc cations in the crystal changes the morphologies in substituted samples. The average particle size remained nearly constant and approximately within the range of 170–190 nm. It is observed however that at concentration x = 0.5 of cobalt and nickel the particle size decreases due to existence of secondary phases. It is observed that substituted hexagonal ferrites $Ba_{1-x}Sr_xCo_2AlFe_{15}O_{27}$ (with x = 0.2, 0.4, 0.6, 0.8 and 1) has grains like platelets with hexagonal shape with grain size of about 2.75–2.69 mm. The reported $Ba(MnZn)_{0.3}Co_{1.4}Fe_{16}O_{27}$ exhibit hexagonal structure with flakes. The average grain size was about 5 ìm with a narrow size distribution. MnZn substitution in less concentration does not significantly affect the grain size and morphology. The suitable amount of doping helps in increasing the microwave loss of the ferrites.

Magnetic Properties

The magnetic characteristics of materials largely lean on the particle size. For hexagonal ferrites, the critical size for particle in the single domain is nearly less than 1 μm. If the particle size is greater than critical size then they would exist in multiple domains. The enhacement in sintering temperatures can make the particles go in the critical single domain size which enhances the saturation magnetization (Ms), retentivity (Mr) and coercivity (Hc). The increase in Ms, Mr and Hc is due to rotation of spins in the single domain. It is observed that these values of saturation magnetization, coercivity and retention start to decrease due to increase in particle size at higher temperatures. If $Mr/Ms \geq 0.5$, it indicated single magnetic domain and if the ratio $Mr/Ms \leq 0.5$ then compound is in multi magnetic domains.[41] The applications of hexagonal ferrites due to their magnetic properties are classified in two categories. The first category belongs to high frequency electromagnetic signal matching and EM energy conversions. The material needs to have high real permeability and low loss. The second category is attenuation and high frequency EM wave absorption. Here the material ought to have high magnetic loss. It is noted that for both categories low permittivity and conductivity are required.[42]

The coercivity of hexagonal ferrite depends on many factors, like particle size, porosity of the material, crystal structure, composition, structure and magnetic anisotropy. It is observed that morphology strongly affects coercivity.[43-44] The saturation magnetization and magnetic anisotropy change due to change in particle size and chemical composition. The investigation of $CaSr_2(MnZn)_{x/2}Fe_{16-x}O_{27}$ with (x = 0 to 1) yielded enhanced hard magnetic property with reduced particle size.[27] The coercivity values increase with addition of Al^{3+} ions as dopant in $BaCoZnFe_{16-2y}Al_yCe_yO_{27}$ (y = 0, 0.2, 0.4, 0.6, 0.8 and 1.0), it reported increased coercivity values due to increase in the anisotropy along c-axis, which is the easy axis of magnetization in W-type hexaferrites.[45] The doping of MnZn in barium-cobalt ferrite $Ba(MnZn)_xCo_{2(1-x)}Fe_{16}O_{27}$ (x = 0.1, 0.2, 0.3, 0.4 and 0.5) results in magnetic loss caused due to magnetization relaxation, domain wall resonances.[12]The levels of doping of MnZn results in better impedance matching which can be beneficial in wide band microwave absorber. The study and synthesis of W-type hexaferrites nanoparticles of $SrZn_{2-x}Co_{x/2}Ni_{x/2}Fe_{16}O_{27}$ (x = 0–0.5) reveal that with enhancement in the concentration of dopant, saturation magnetization and remnant magnetization also increase. This can be because of site preference of zinc, cobalt and nickel cations in the structure of W-type ferrite. The occupancy if the seven sublattices of the W- type ferrite by the divalent cations after doping decides its magnetic properties. The hysteresis loops and magnetic measurements reveal that coercivity decreases and saturation magnetization increases with the substitution of Ni and Co upto the concentration value x = 0.4. [15] Rare earth ions when doped in the structure of W-type barium hexaferrite influences the magnetization of all sublattices and the magnetic moments. [46] Temperature dependence of magnetization in W-type hexaferrite is an area which can be explored extensively. We are aware that coercivity depends on the properties of the material like crystal structure, chemical composition, grain size, porosity, defects etc. The temperature variation can affect the coercivity to a great extend due to changes in the anisotropy and microstructures. When the magnetic properties of $Ba_{1-x}Sr_xCo_2AlFe_{15}O_{27}$ (x = 0.2–1.0) was studied as a function of temperature, the samples exhibited strong magnetism. The coercivity was found to be low and saturation magnetization got enhanced. [16] It was observed that with rise in temperature of the Co_2W compound, saturation magnetization decreases linearly. The linear fall in the saturation magnetization with rise in temperature is due to the disorientation in the alignment of magnetic moments due to thermal energy which decreases the components along direction of net magnetization. It has been observed that for elevated temperatures, there is increase in saturation magnetization and decrease in coercivity of the W-type hexaferrite. The increased value of permeability and magnetization enables W-type ferrite to be a potential and a suitable material for RAM and other applications. These temperature dependent magnetic properties make these materials useful for various applications. It has been seen that reduction in the particle size to nanoscale can modify the crystal structure to single domain which enhances the coercive force leading to large hysteresis attenuation.[47] The synthesis of polycrystalline $CaMg_2Fe_{16}O_{27}$ by substituting divalent Mg^{2+} ions results in increased magnetic moment and reduced coercivity. The magnetization is found to be greater with substitution of Mg^{2+} ions than the substitution of Cu^{2+} and Co^{2+}.[48] The divalent Mg^{2+} ions have a preference for tetrahedral sites which belongs to the spin down orientations As a result of which this substitution lowers the magnetic moment of these sub lattices, thereby increasing the total magnetic moment. The substitution of Mg^{2+} ions on the tetrahedral sites in $BaCoZn_{1-x}Mg_xFe_{16}O_{27}$ ($0 \leq x \leq 0.6$) W-type structure enhances the magnetic properties.[19] It has been reported that with enhancement in the concentration of Mg^{2+} ions, the magnetic intensity as well as the magnetic susceptibility fall which in turn decreases the net magnetic moment. The reflection on the magnetic properties of the studied composition $Ba_1Co_{0.9}Zn_{1.1}Fe_{16}O_{27}$ and $Ba_{0.8}La_{0.2}Co_{0.9}Zn_{1.1}Fe_{16}O_{27}$ yields subsequent enhancement in magnetic losses by partial substitution of La^{3+} for Ba^{2+} ions. [47] The doping of Zn^{2+} ions at the tetrahedral sites in the series $SrZn_{2-x}Co_xFe_{16}O_{27}$ ($SrZn_{2-x}Co_x$-W) at 298 K and 6 K results in the lowering of the magnetic moment of the minority sublattice and hence enhancement in total magnetic moment. It has also been reported that substitution of Co^{2+} substitution has a strong influence on the magneto-crystalline anisotropy at room temperature and at 6 K. [49] The reported synthesis of calcium hexaferrites($CaFe_{12}O_{19}$) with the substitution of Zr^{4+} and Co^{2+} ions x=0 to x=4 yields a decrease in the saturation magnetization (Ms), retentivity (Mr) and coercivity (Hc). This decrease is due to diamagnetic ions occupying spin up and spins down sublattices.[50] A majority of hexagonal ferrites have a uniaxial anisotropy along the easy axis. The inclusion of small amount of cobalt ion in the lattice of hexaferrites gives rise to the reorientation of the magnetization vector and hence increase of magnetic properties.

Curie Temperature

Above a certain temperature called the ferrimagnetic Curie point, the material turns from ferrimagnetic to paramagnetic. The Curie point is usually lower in ferrites than for the ferromagnetic substances (for example: 520 °C for $CoFe_2O_4$, 440 °C for $MgFe_2O_4$). It has been seen that when rare-earth ions are doped into barium W-type hexaferrite the Curie temperature rises with increasing rare-earth ionic radii till it reaches maximum value at the ionic radius(≅ 1.04A°), then decreases again. The exchange interaction between oxygen and Fe^{3+} ions increases which enhances Curie temperature. The decrease in the curie temperature later after the increase may be credited to the change in the angle of Fe^{3+} ions and oxygen due to change in ionic radius. It has been generally noted that Curie temperature lowers down with substitution of rare-earth ions in W-type barium hexagonal ferrites. The calcium W-type hexagonal ferrite with composition $CaSr_2(MnZn)_{x/2}Fe_{16-x}O_{27}$ with (x = 0 to 1) has reported the curie temperature in the range of 473K to 498 K.[16] The observed diamagnetic substitution of Mg^{2+} in Calcium W-type hexaferrite increases the curie temperature due to variation in the arrangement of spins in the composition. In barium W-type ferrite $BaCoZn_{1-x}Mg_xFe_{16}O_{27}$ $(0 \leq x \leq 0.6)$, the substitution of Mg^{2+} instead of Zn^{2+} ions with the ratio more than 50% increases the Curie Temperature due to variation in the angle and superexchange interaction. The enhancement in the concentration of Mg^{2+} beyond x=0.5 reduces the Curie temperature without any change in valency distribution. In ferrimagnetic $SrCo_2Fe_{I6}O_{27}$ the substitution of Zn^{2+} ions weakens the superexchange interactions leading to decrease of the Curie temperature. The doping of cobalt in the same Sr-W-type structure reflects opposite dependence of Curie temperatures.

Reflection Loss

The reflection loss (RL) can be defined in terms of the permittivity år and permeability μr measured at the given frequency and absorber thickness using the following equations:

$$Zin = \sqrt{\frac{\mu r}{\varepsilon r}}\, th\left(\frac{i.2\pi fd\sqrt{\mu r\varepsilon r}}{c}\right) \qquad ....(1)$$

$$\text{RL} = 20\log\left|\frac{Zin-1}{Zin+1}\right| \ (dB) \qquad ....(2)$$

Zin= Input Impedance

RL= Reflection Loss in decibels (dB).

f = Frequency of Microwave

d= thickness of the absorber

c= Velocity of light in free space

The reflection loss (RL) of the samples is according to the transmission line theory.[51] At an impedance mismatch, reflection loss is the ratio of the incident power to the reflected power. Reflection loss is usually expressed in dB. The electromagnetic wave absorption ability or capacity of the material is evaluated by calculating the reflection loss. For radar applications, the reflection loss of less than -20 dB is nearly 99 % of the microwave absorbed by the material and that less than -10 dB is nearly 90% of the EM absorption. It has been noted that , the reflection loss value for W-type $BaCoZnFe_{16}O_{27}$ $(BaCoZnFe_{16-2y}Al_yCe_yO_{27})$ with substitution of a combination of Al^{3+} and Ce^{3+} is found to be -22.5 dB at Al–Ce concentration of y = 0.4 at thickness of 4.59mm with peak value at 8.5 GHz. More than 99% absorption was observed at concentrations y = 0.2 and y = 0.4 which is because of low permittivity and high permeability after doping.[39] For W- type hexaferrite $Ba(MnZn)_xCo_{2(1-x)}Fe_{16}O_{27}$ doped with MnZn, the reflection loss is maximum of -40.7 dB at a frequency of 7.3 GHz. When the thickness of the sample was 2.8 mm and x = 0.4, it has been reported that the reflection loss is maximum in the bandwidth of 6.6 GHz for losses less than -10 dB.[12] The doping of MnZn if found to affect the absorption properties. W-type hexagonal ferrites nanoparticles of $SrZn_{2-x}Co_{x/2}Ni_{x/2}Fe_{16}O_{27}$ (x = 0–0.5)exhibited maximum reflection loss of -29.11 dB at 14.57 GHz with 6 GHz bandwidth through the frequency range of 12–18 GHz for absorber thickness of1.8 mm as per the literature.[15] Thus, it can be stated that the substitution of Ni, Co and Zn in W-type hexaferrite can control the reflection loss and hence modifications desired in reflection loss characteristics can be achieved. The magnetic and microwave characterization of single phase hexaferrites of composition $Ba_{1-x}Sr_xCo_2AlFe_{15}O_{27}$

(x=0.2–1.0)for application in a microwave absorber, have been reported.[16] The reflection loss of -20dB for the frequency range 1.61 GHz was obtained with minimum loss of -36.82 dB with thickness of sample 2.3mm. This indicates that change in absorber thickness can modify the minimum reflection loss. From the citations it is observed that ZnCo-substituted W-type barium hexaferrite at the nanoscale gives maximum reflection loss of -28.5 dB; for a reflection loss above -10 dB, the bandwidth is about 5 GHz compared to only 3.5 GHz.[46] The study on $Ba_1Co_{0.9}Zn_{1.1}Fe_{16}O_{27}$ and La^{3+} substituted W-type barium-hexaferrite with composition $Ba_{0.8}La_{0.2}Co_{0.9}Zn_{1.1}Fe_{16}O_{27}$ reflected the reflection loss below -10dB for bandwidth 8 GHz. The peak value of reflection loss is about -39.6 dB when the absorber layer thickness is only 2mm.[48] Hence, by suitable substitution the reflection loss peaks can be modified and the reflection loss characteristics can be influenced for enhancing microwave absorption properties.

Microwave Absorption

Due to rapid advancement in Information and communications technologies, electromagnetic (EM) waves carry information at a faster rate. EM wave absorbing technology is gaining prominence due to high demands in miniaturization and performance of antenna. [52] There are wide range of applications in the lower frequency bands of microwaves ranging from 1 -18 GHz. Radio satellite communication, GPS, Broadcasting radars, wireless cell phone networks are extensively using microwaves in Gigahertz frequency range. With the extensive development in electronics there is a need to curb Electromagnetic Interference which poses many problems. The reduction in size and thickness of the electronic devices and components bring about a destructive and undesirable influence on the reliability and effectiveness of the electronic systems. With the fast development of wireless communication technology, EM interference caused health hazards and threats the security of information. [53] This led to research in exploiting different types of materials with high performance light in weight EM wave absorption with miniaturization. The compatibility and efficiency of electronic systems decreases due to unwanted reflections and emissions of EM waves. The issue can be resolved by designing the microwave or EM problem which can suppress the reflection and reduce the free-space EM waves. The energy of the EM wave is converted into other forms like thermal energy or the wave is removed by phenomenon of interference so that reflection and emissions can be minimized. Electromagnetic wave absorbers should have very strong magnetic loss as well as dielectric loss properties. This is essential for the EM wave to get attenuated inside the material. The role of impedance matching is also crucial for the absorption process. The inherent impedance of the material to be used should be made equal to the free space. The permittivity 'å' and permeability 'µ' of the material are needed parameters to be analyzed for electromagnetic absorption. The synthesis techniques and particle size of the materials decide their magnetic and dielectric properties which very much affects the microwave absorption property. For better performances of the absorbing designs the calculations of frequency bandwidths are undertaken as per the applications. This is useful in stealth technology and for wireless communication systems. For Radar applications, wider frequency bandwidths are required. Reflection loss (RL) is one such parameter to evaluate the Electromagnetic Absorption capacity of the material. For wider frequency band and frequency absorption at various values, a mixture of dielectric and magnetic absorber is taken. The grain size also plays an important role in modifying the electromagnetic absorption properties.

The synthesis of barium W-type hexaferrite partially substituted with zinc and rare earth La^{3+} has been found to enhance the microwave absorption properties with bandwidth of 8 GHz below -10dB at the absorber film thickness of about 2 mm only. The military aircrafts and vehicles have their surfaces usually coated with microwave absorbers for enhancing the concealing properties.[51] For such absorber coats there is a need for materials having high relative permeability. It has been reported that nanoscale preparation of W-type Barium hexaferrite reduces absorber coat thickness with better bandwidths. So, microwave absorbing properties of nanocrystalline materials can be explored for better prospects. An ideal microwave absorbing material requires wide bandwidth, less reflection loss and less impedance matching thickness. The research on finding and synthesizing such materials with good microwave absorbing properties is still in progress. The characteristics of impedance matching and attenuation of EM wave are two important things for low-reflecting absorber for a desired frequency for a finite thickness of the absorber.[55] Out of all the hexagonal ferrites of similar crystal structure W-type hexagonal ferrites have better microwave absorbing properties which should be explored for future applications. $Ba_{1-x}Sr_xCo_2AlFe_{15}O_{27}$ (x=0.2–1.0) gives the reflection loss of -36.82 dB and for a bandwidth of 1.61GHz a reflection loss of -20 dB at thickness 2.3mm.The magnetic relaxation and resonance of domain walls in the reported synthesis of $Ba(MnZn)_xCo_{2(1-x)}Fe_{16}O_{27}$ becomes the reason of microwave absorption. At a thickness of 2.8 mm, the loss of less than -10dB at the bandwidth of 6.6 GHz and the minimum reflection loss of -40.7 dB at the frequency of 7.3 GHz for MnZn doping was observed. The W-type material sample exhibited soft magnetism, the properties of which can be altered by proper doping concentrations for desired microwave absorption. It has been seen that the doping of rare-earth ions into the structure of W-type hexaferrite improves the electromagnetic absorption properties over the wide range of frequencies. W-type hexagonal ferrites nanoparticles of $SrZn_{2-x}Co_{x/2}Ni_{x/2}Fe_{16}$ (x = 0–0.5) obtained by co-precipitation method gives satisfactory values of reflection loss for use in the Ku-band frequency range by changing the substitution values of Ni, Co and Zn cations. The W-type hexaferrite $BaCoZnFe_{16-2y}Al_yCe_yO_{27}$ (y = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) synthesized by the chemical co-precipitation method gives minimum reflection loss of -22.5dB at the frequency bandwidth of 8.5GHz for thickness of 4.59 mm for varied values of Al^{3+} - Ce^{3+} content. If the thickness of the absorber is varied in these compounds for the desired frequency range cab tune the microwave absorbing characteristics. Due to this, the nanoparticle synthesis and study of these compounds in the frequency bandwidth of 0.5-10 GHz range is done for potential applications. A good microwave absorbing material can be coated on metal plates of tanks, aircrafts and ships to suppress reflections and increase attenuation.

CONCLUSION

The suitable amount of substitution and the variations in morphology are useful in enhancing the electromagnetic loss of the ferrites. Microwave absorbers devices in GHz frequency range, with desired reflection losses could be obtained by controlling the compositions of various dopants in the W-type hexaferrite. Following are the observations:

1. It has been generally noted that Curie temperature lowers down with substitution of rare earth ions in W-type barium hexagonal ferrites. The substitution of Zn^{2+} ions weakens the superexchange 'interactions decrease the Curie temperature. The substitution of cobalt in the same Sr-W-type structure reflects opposite dependence of Curie temperatures.
2. The grain size also plays an important role in modifying the microwave absorption properties. With the substitution of Ni, Co and Zn in W-type hexaferrite can control the reflection loss and hence modifications desired in reflection loss characteristics can be achieved. The W-type material sample exhibited soft magnetism, the properties of which can be altered by proper doping concentrations for desired microwave absorption. It has been seen that the doping of rare-earth ions into the structure of W-type hexaferrite improves the electromagnetic absorption properties over the wide range of frequencies. W-type hexagonal ferrites have better microwave absorbing properties which should be explored for future applications. The synthesis of barium W-type hexaferrite partially substituted with zinc and rare earth La^{3+} has been found to enhance the microwave absorption properties with bandwidth of 8 GHz below -10dB at the absorber thickness of about 2 mm only. The results mentioned suggest that these ferrites have potential applications as microwave absorbers in the broad bands, switching devices and sensing applications.
3. The synthesis of polycrystalline $CaMg_2Fe_{16}O_{27}$ by substituting divalent Mg^{2+} ions results in increased

magnetic moment and reduced coercivity. The magnetization is found to be higher due to substitution of Mg^{2+} ions than the substitution of Cu^{2+} and Co^{2+}. It has been reported that with rise in the concentration of Mg^{2+} ions, the magnetic intensity as well as the magnetic susceptibility decreases which decreases the net magnetic moment.

4. It has been reported that with the doping of nickel and cobalt ions instead of zinc ions in the lattice, the morphologies vary from irregular plate-like in pure samples to hexagonal pyramidal shapes in doped samples.

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APPENDIX

Nomenclature

dB	Decibel
εr	Relative permittivity (ε= permittivity, or dielectric constant)
μB	Bohr magneton
μr	Relative permeability
ρ	Density
GHz	Giga Hertz
RL	Reflection Loss
c	Velocity of light in free space
Tc	Curie temperature
VSM	Vibrating sample magnetometer
W	$BaMe_2Fe_{16}O_{27}$ ferrite
Wb	Webber, SI unit of magnetic flux
XRD	X-ray diffraction
K	Kelvin
Ms	Saturation magnetization
Mr	Remanence
Hc	Coercivity
Oe	Oersted
T	Tesla
EM	Electromagnetic
SEM	Scanning Electron Microscopy