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Chapter

Development of Graphene Based Cobalt-Ferrites Nanocomposites for Microwave Shielding

Muhammad Siyar and Asghari Maqsood

Abstract

The study is related to cobalt ferrites nanocomposites embedded with graphene nanosheets, prepared by co-precipitation method. Various doping of graphene from 0.1% up to 1% were applied within the cobalt ferrite structure to study its microwave and mechanical effects on the nanocomposites. Microstructural analysis confirms the homogeneous dispersion and successful adhesion of graphene nanosheets within the cobalt ferrite matrix. Microwave absorbing capacity of these samples was studied by Agilent network analyzer in low frequency band of microwave (1MHz to 2 GHz), Results reveals that graphene incorporation not only improved the absorption capacity of cobalt ferrites (13dB-17d), but also widened its maximum absorption peak. This change was supposed to be due to inhomogeneity and combine effects of electric (graphene), and magnetic dielectric nature (cobalt ferrites). Further mechanical characterizations reveal that our composites samples have higher flexural strength (19.92 MPa for 1% loading) and improved toughness (>6000 J/mm2) compare to pure cobalt ferrites (10.28 MPa, 1000 J/mm2).

Keywords: Cobalt ferrites, nanocomposites, graphene, microwave shielding

1. Introduction

1.1 Introduction to ferrites

Ferrites are the magnetic mix metal oxides comprising the ferric ions as an essential constituent, while in mineralogy or in metallurgy the term ferrites refer to that material having a cubic crystal structure of spinal mineral. The ferrites application has been known from ancient times for multiple centuries. Magnetite or ferrous ferrite is a naturally occurring ferrite. These are a class of mix metal magnetic oxide materials where ferric ions are present as a basic constituent. In metallurgy or mineralogy any materials containing spinal mineral of cubic crystal structure is referred as ferrites. The Chinese found its use in the loadstone (i.e. Fe_3O_4) due to its weak permanent magnetism for navigation purposes as early in the 12th century [1, 2].

Hilbert a German scientist, in 1909 reported first systematic study on the relation between magnetic and chemical properties of many iron oxides, but faced hurdles to identify its magnetic phases. However near to 1930s modern ferrites were

investigated by Forestier, Hilppert and Wille for their structural, magnetic and electrical properties. Japanese scientist's attempted to study magnetic oxides from 1930s to 1935, Snoek and co-workers were studying the ferrites in 1936; they found that one of the important properties of ferrites to use as core for inductors is the loss tangent per permeability, so called loss-factor (**Figure 1**) [3].

They also investigated that loss can always be minimized by introducing an air gap and the permeability not effected adequately. This finding, led Snoke to develop manganese-zinc ferrite, of low loss and ultimate permeability. It was 1945, that Snoke coined the physical and technological applications of modern ferrites and a new field of science came into being. Since that time ferrites brought stormy revolution in electrical and electronic areas, to improve its capability and endurance [4–6].

1.2 Structure of ferrites

Ferrites crystallize in three types of structures.

Garnet Ferrites: These are also cubic structural ferrites but with general formula $Ln_3^{3+} Fe_5O_{12}$, here Ln maybe, EU, Tb, Tm, Ho, Er, Gd or Ln [7].

Magnetoplumbit ferrites: With hexagonal structure, having general formula $M^{2+} Fe_{12}O_{19}$, where M may be Sr. or Ba [8].

Spinal ferrites: Having cubic crystalline structure with general formula $M^{2+} Fe_2O_4$, here M may be any metal such as Mn, Cd, Fe, Co, Cu, Mg or Al [9].

Spinal ferrites are the simplest structure, crystallizes among the three ferrites groups. The spinal ferrites unit cell is comprised mainly of oxygen lattice, having 32 oxygens, 16 trivalent irons along with 8 divalent metal ions, as shown in **Figure 2**. An interesting feature of oxygen lattice is its ions are arranged in face centered cubic structure, such that two types of interstitial sites are produced, at A site tetrahedral co-ordinate and octahedral B sites. The whole unit cell consists of two groups of four cubes. The positions of the ions are changing in these groups may share corners, faces or edges. Each group having four oxygens (Large spheres), located diagonally on each accountant and also on the tetrahedral corner. The tetrahedral oxygen ions surrounding the metal ions located in the center of the left hand side octant (small sphere, not shaded). This ion appeal to occupy A site of the intrinsic position produced by oxygen.

The second ionic group on right hand contains four metal ions enclosed by an octahedron resulted from six oxygen ions, and goes to fill the B site. Hence each unit cell consists of 64 A sites, only 8 of which are occupied and remaining unoccupied free sites. B sites are 32 in number, 16 of which are occupied [4, 5].

Figure 1.
Ferrites devices used in different applications [1]. It can be easily made in any design and shape, and hence give it more diversity to be applied in various magnetoelectric applications.
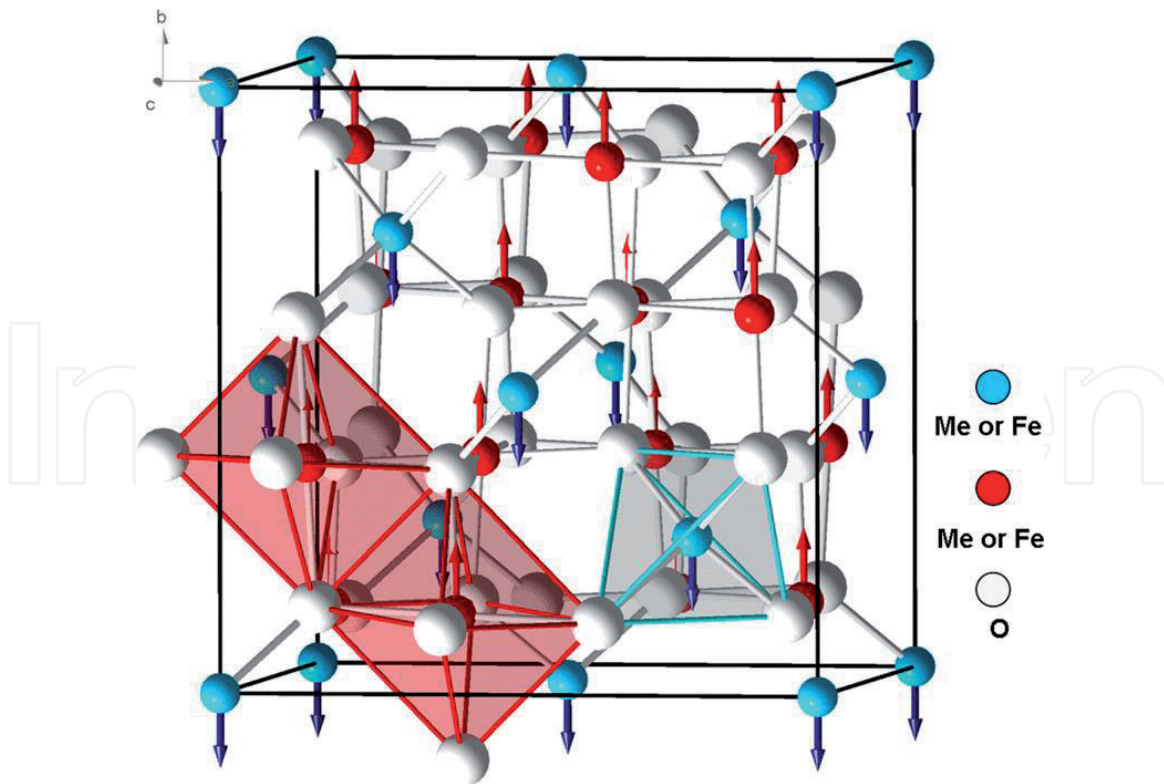
Figure 2.
Structure of spinal ferrite unit cell, comprised mainly of oxygen lattice, having 32 oxygens, 16 trivalent irons along with 8 divalent metal ions [5].

1.3 Synthesis routes of ferrites

As we are interested in ferrites composites, so we have to evaluate nano ferrites synthesis techniques, while coarse ferrites are produced by traditional ceramic processing. Nano particles ferrites are superior due to large surface area, very small size, high surface energy and excellent properties [9, 10].

Bottom –up and top-down approaches are reported so far, in bottom-up we take molecules or atoms to manipulate these in a systematic way to get the desired shape, size and properties of specific ferrite materials. In top-down approaches the bulk materials are broken down repeatedly until we get nano sized materials. Mechanical attrition done in high energy ball milling is an example of top-down approach.

Synthesis routes may be generally classified in two ways, the physical way (involving only physical changes such as phase, shape, and size of the matter) and chemical way (where permanent or chemical change occurs). Bottom-up techniques as lithography, ball milling and screen printing are all physical synthesis routes. Some chemical routes for nano ferrites synthesis are sol–gel, hydrothermal and co-precipitation reported from various laboratories [11, 12].

Maaz et.al reported the successful synthesis of cobalt ferrites nano particles via wet chemical route. In this study they have studied CoFe2O4 nanoparticles in the nanometers range size for low saturation magnetization and large coercivity. They succeeded to achieve an efficient control over the size of the synthesized cobalt ferrite particles via finely tuning the annealing temperature and time [13].

we have presented the synthesis of CoFe2O4 nanoparticles in the range 15–48 nm. The size of the nanoparticles was measured both by XRD and TEM and were in very good agreement with each other indicating that there was no agglomeration and that the size distribution of the prepared nanoparticles was small. The size of the nanoparticles appeared to increase linearly with annealing temperature and time most probably due to coalescence that increases with increasing

temperature of anneal. It is evident that particle size and its distribution may be controlled both by controlling the rate of reaction and the annealing temperature and time. The very large coercivity and low saturation magnetization at 77 K in comparison with room temperature appear to be due to a pronounced growth of magnetic anisotropy at low temperatures. The observed magnetization remanence ratio of 0.47 at room temperature (very close to the value of 0.5 typical of a system of noninteracting single domain particles) suggests that $CoFe_2O_4$ nanoparticles exhibit an effective anisotropy that is uniaxial. The effective uniaxial anisotropy in magnetic nanoparticles has been explained as arising from surface effects that also lead to large anisotropy energy in nanoparticles. The coercivity shows a peak with particle size at a value much smaller than the single domain limit and is attributed to the onset of thermal effects at small enough particle sizes. We find that for smaller particles the saturation magnetization had a value that was significantly lower than the bulk value while the larger size particles have values approaching those of the bulk. The smaller value of MS in smaller particles is attributed to the greater fraction of surface spins in these particles that tend to be in a canted or spin glass like state with a smaller net moment.

1.4 Properties and applications

Ferrites are used in almost every electrical and electronic devices, it finds its use in the applications from simple lifting magnets to complex electrical and communication systems. Demand for ferrites is increasing rapidly due to the advancement in modern technology, such as satellite communications, radar systems, memory, and advance computer applications. The major upsurge for the passion of ferrites research is due to the development of modern small and fast power supplies, which are being used in cell phones, computers, communications, microprocessors, and entertainment applications [14].

Ferrites coined its modern use, first in a powerful application to enable the time dependent magnetic deflection of the electron array, in a television receiver. Mn-Zn ferrite emerged as an excellent candidate for core material in line-time-base and e.h.t transformer. Another excellent area of use was the field-shaping the yoke for beam deflection system in the picture tube. Later on, several ferrites' compositions i.e. Mg-Zn, Ni-Zn and Li-Zn etc. were applied for yokes application due to higher resistivity to enable direct winding of the coils on ferrite. However highly efficient TV deflection yokes are fabricated from Mn-Zn ferrite. Also, ferrite rods and plates make it possible to make the compact antennas for radio receivers (**Figure 3**) [12–14, 16].

The need for use of ferrites in line communication systems started, when the analog frequency divisions multiplex (FDM) systems demand for large numbers of ultimate performance, transformers and inductors operating in the frequency range from 40 kHz to 500 kHz. Ferrites were selected an excellent agent for core materials in these applications, due to a combination of high resistivity along with good magnetic nature. Their large frequency range along with ultimate resistivity successfully replaced the conventional metallic magnetic materials and further enabled FDMs to operate over wide and higher frequency range [17].

Other important applications of ferrites are summarized below.

- Flyback transformers [18]

- Fitter inductors [15]

- Magnetic amplifier [19]

Figure 3.
Digital TV receiver contains Mn-ferrites deflection yokes [15].

- Antenna cores

- IF transformers

- Magnetic switches and memories

- Magnetic drug delivery systems.

2. Materials and methods

Graphene based cobalt ferrites nano composites were prepared by facile co-precipitation route [20]. Homogeneous solution was first prepared by mixing appropriate amount of Fe (NO3)3.9H2O and 0.1 mol of Co (NO3)2.6H2O in deionized water followed by vigorous mixing. Appropriate amount of GO loading was applied to achieve 1%, 0.5% and 0.1% loading in respect to ferrite precursors. The prepared homogeneous mixture was stirred continuously and heated up to 95°C, while NaOH salt was added drop by drop. The process of mixing at the set temperature was continued for around 3 hours to obtain the dark black solution. After completion of reaction the solution was washed and filtered with the help of centrifuge again and again to get the neutral PH and remove the reaction media and impurities. Composite samples were dried in oven at 80 C for 24 hours and sintered for 3 hours at 700°C. Characterizations.

XRD spectra were recorded for all the samples in two thetas range from 10 to 70, on the pellet samples. Both the permeability and permittivity of our samples were measured by Agilent RF Impedance-Material analyzer (moel-E4991A), over the entire range from 1 MHz to 3GHz, with using 16453A test fixture for permittivity and 16454A for permeability on normal and torrid samples, respectively.

3. Results and discussion

3.1 Phase analysis of composites

Ferrite nano composites samples were analyzed by X-ray diffraction to study the structure and phases of the obtained samples. The obtained XRD spectra of all the

samples maybe seen in the **Figure 4**. The corresponding planes (531), (440), (511), (422), (400), (222), (311), (220) and (111) have observed in all the samples, which confirm the successful formation of ferrite structure. Presence of graphene can be seen only in 1% graphene doped sample at 28 degrees two theta, while in other samples graphene amount were not enough to be reflected in the XRD spectra.

3.2 Electrical characterization

The microwave composed of two perpendicular magnetic and electrical vectors [21], as shown in **Figure 5**.

So efficient absorption can only be achieved by canceling both the electrical and magnetic components of it. When we use some media for microwave absorption, it should be capable of opposing both these perpendicular vectors. Here we want to study the absorption of microwave by incorporating electrically conducting graphene sheets into magnetic (cobalt ferrites) matrix.

3.3 Real permittivity and permeability

The behavior of frequency dependence of the real parts (ε' and μ') of permittivity and permeability for cobalt ferrites (S0) and its composites with different loading of graphene (S1, S2, S3) at room temperature is shown in **Figure 6**. As is clear from this study that all the samples exhibit frequency dependency for both permittivity and permeability in the low frequency range which become independent of frequency at higher frequency and shows consent behavior with respect to it. The variation of ε' with respect to change in composition may be explained by Maxwell-Wagner theory of space charge polarization [22]. Due to the inhomogeneous structure composed of good conducting grains and poor conducting grain boundaries of dielectric materials
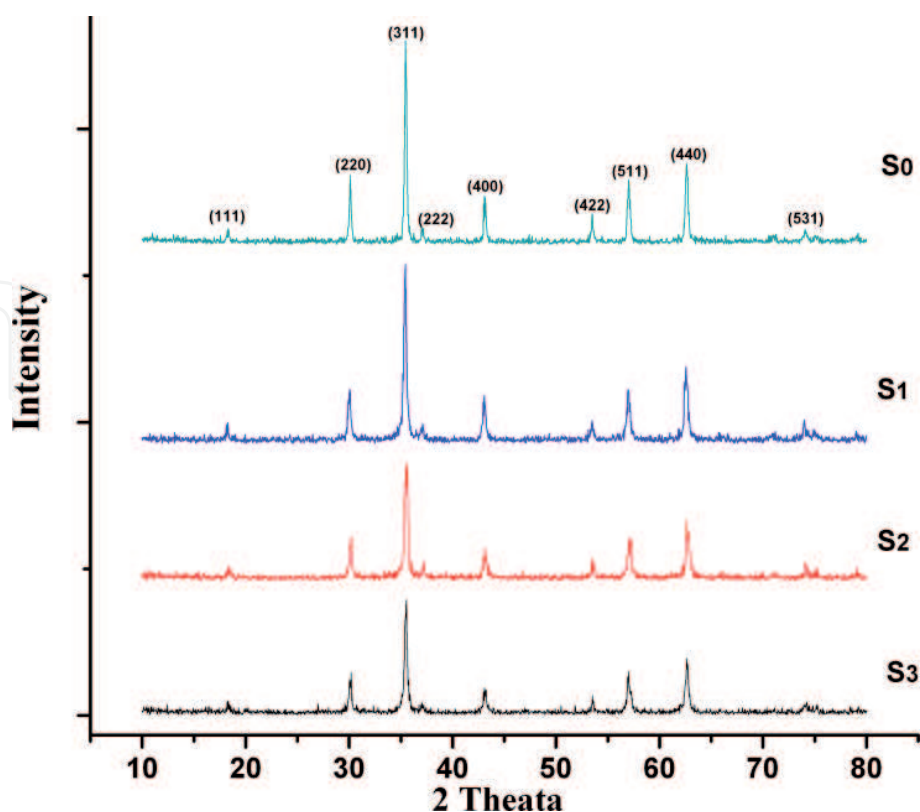

Figure 4.
XRD spectra of graphene based cobalt ferrites nano composites prepared by facile co-precipitation route. S₀ is pure ferrite while S1, S2 and S3 refers to the appropriate amount of GO loading of 1%, 0.5% and 0.1% in ferrite matrix.
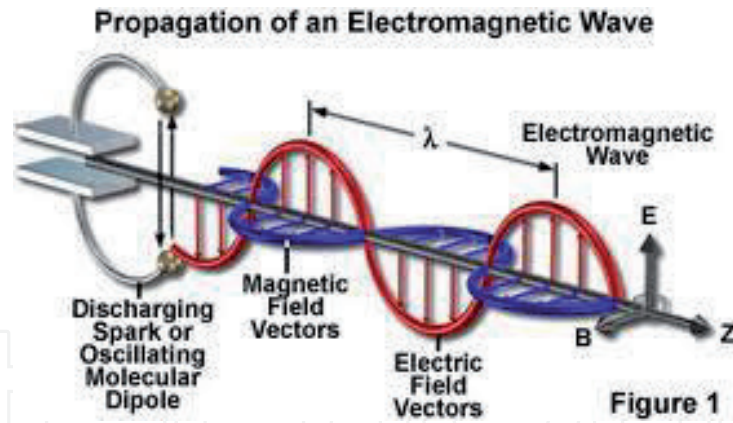
Figure 5.
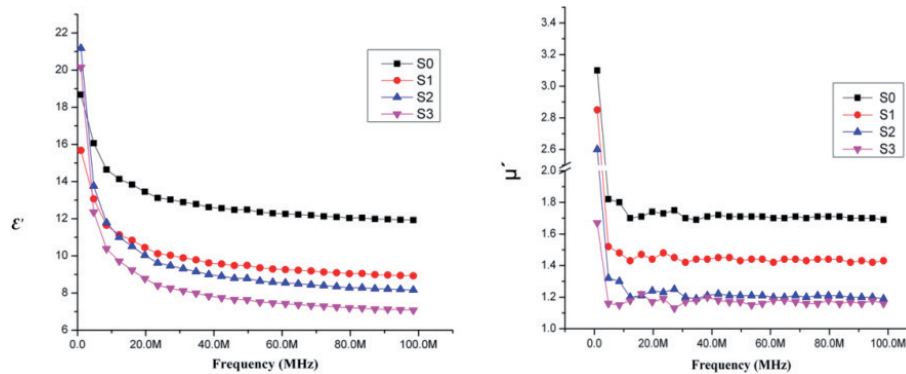*Schematics for the demonstration of electromagnetic wave propagation and its various vectors.*

Figure 6.
Real part of permittivity and permeability of Co nanoferrite and composites samples in the frequency range of 1 MHz to 100 MHz.

space polarization occurs. In more detail the electrons are approaching to the grain boundaries passing through the conducting media within the grain by hopping, piled up along the boundary lines and produced polarization [23].

When the applied field frequency is increased the probability of electron approaching towards grain boundaries decreases and hence dielectric constant also goes down. For composite samples the lower curves are due to the conducting graphene sheets in between the cobalt ferrite particles, which tend to decrease polarization due to conduction of charges along these conducting sheets.

3.4 Complex permittivity and permeability

Complex spectra for permittivity and permeability are taken for all the composites and pure cobalt ferrites samples in the frequency range up to 100 MHz are shown in **Figure 7**. Both imaginary parts of permittivity and permeability refer to the energy loss from the material to the electric and magnetic field respectively [24]. For permittivity the complex portion is highly dependent on the frequency of all the four samples and decrease rapidly with increasing frequency which becomes less dependent after 50 MHz if we compare the responce of cobalt ferrites to its composite samples, it can be seen from the **Figure 6**. That at the start composites samples has higher loss than the pure ferrites while going at higher frequency the loss became higher for ferrite sample comparable to all other composites. Although there is some gap in the response of ferrites and composite samples but it is negligible and hence we can assume that no major affect is there in ferrites loss to electric field due to graphene incorporation. This decrease may be due to the presence of comparatively
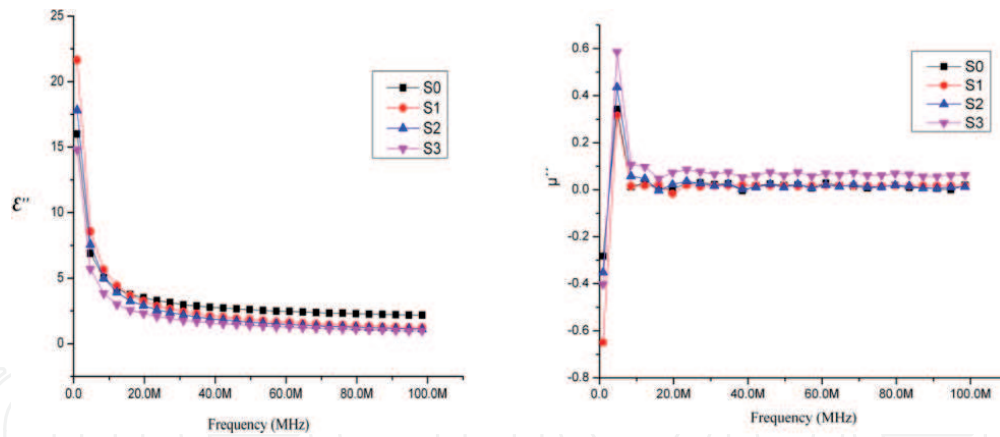
Figure 7.
Complex parts of permittivity and permeability of Co nanoferrite and composite samples in the frequency range of 1 MHz to 100 MHz.

low magnetic and dielectric graphene sheets [25]. Considering the spectra of complex permeability with respect to frequency as shown in **Figure 7**. We have some oscillating response from the zero mean point at lower MHz for all the composite samples which became stagnant at higher frequency. While cobalt ferrite has some rapid decrease and then became independent of higher frequency. The oscillatory response of composites is due to the presence of ferromagnetic nature of graphene sheet in cobalt ferrite matrix, at the start due to low incident frequency the magnetic field is not reflected hence negative values are recorded for loss of magnetic field by the samples. At higher frequency the ferrite response is dominated and goes up to some higher value then comes down and became linear in further frequency range. But again the overall response to magnetic loss is the same for all the four samples.

3.5 Microwave absorption

The reflectivity curves in the frequency range up to 3 GHz for RGO and cobalt ferrite samples are shown in **Figures 8** and **9**, with nearly equal thickness (1.9 ± 0.1 mm).
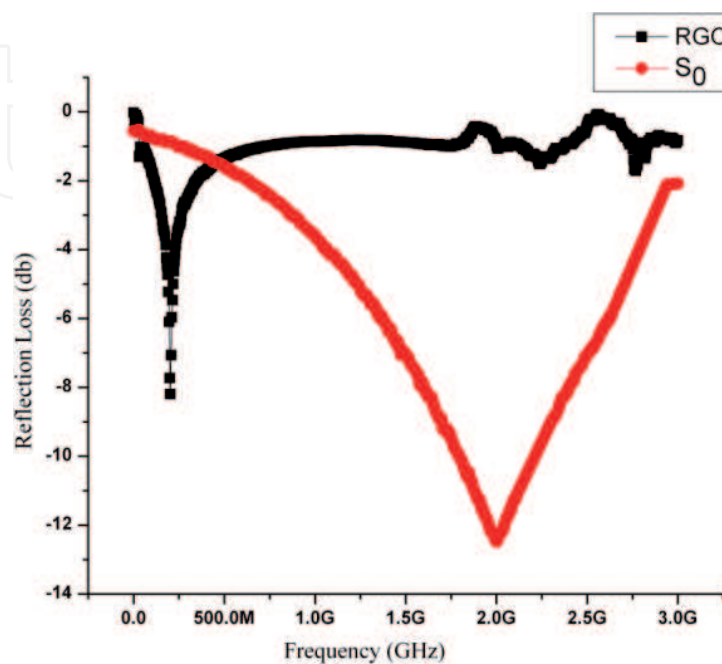

Figure 8.
Microwave absorption curves of cobalt and RGO samples with thickness 1.9 ± 0.1 mm.
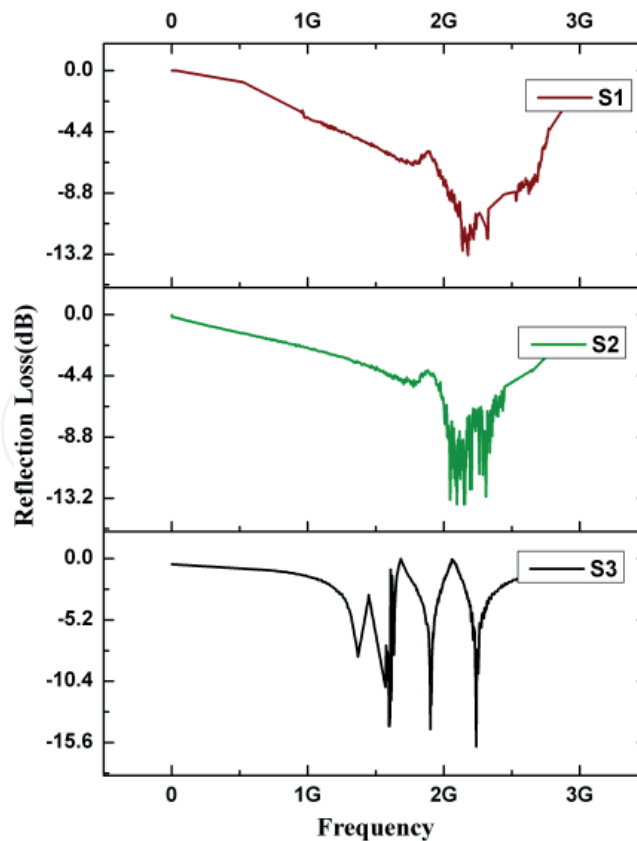
Figure 9.
Microwave absorption curves of Co composites samples with thickness 1.9 ± 0.1 mm.

Maximum absorption peak is reached at nearly 250 MHz at the value up to 9 db, while for ferrites we have greater absorption peak up to 13 db at very higher frequency (2GHz).Absorption spectra of composites samples are shown in **Figure 9**. It is clear that the position and value of absorption peak is not much displaced due to less percent doping of graphene (1%) but is very interesting that parent cobalt ferrite absorption peak is changed into a band of small peaks of nearly equal values.

Moreover as the doping of graphene is increased this band became widen. The reason behind is that single point maxima is converted to band of noise due to inhomogeneity and combine effects of electric (due to graphene), and magnetic dielectric nature (due to cobalt ferrites). So it is finally concluded that graphene based cobalt ferrites composites may be a potential candidate for microwave shielding.

4. Conclusion

In this study we have reported the cobalt ferrites nanocomposites embedded with graphene nanosheets, prepared by co-precipitation method. Various doping of graphene from 0.1% up to 1% were applied within the cobalt ferrite structure to study its microwave and mechanical effects on the nanocomposites. Microwave absorbing capacity of these samples was studied by Agilent network analyzer in low frequency band of microwave (1 MHz to 2 GHz), Results reveals that graphene incorporation not only improved the absorption capacity of cobalt ferrites(13 dB-17d), but also widened its maximum absorption peak. This change was supposed to be due to inhomogeneity and combine effects of electric (graphene), and magnetic dielectric nature (cobalt ferrites). We revealed that

both the electrical properties and conductivity of cobalt ferrites is improved by imbedding very small amount of graphene nanosheet. Along with improving mechanical properties the graphene also widened the microwave absorption band. So, it is concluded that graphene based ferrites composites may play a vital role for microwave shielding applications.

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