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Boosting the Microwave Absorption Properties Using Graphene Functionalized with Mg-Mn-Zn-Bi Ferrites

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ABSTRACT: Graphene (Gr) composites with $Mg_{0.5}Mn_{0.375}Zn_{0.125}Bi_{0.05}Fe_{1.95}O_4$ (*MMZB nano ferrites*), (Gr= 0%, 1%, 2%, 3%, 4%) were synthesized by using the sol gel auto combustion method. XRD, FTIR and Uv-Vis confirmed the significant improvement in structural, vibrational and optical properties of MMZB ferrites\Gr composites with fusion of Gr. The lattice parameter 'a' varies with increasing Gr concertation. From the FT-IR spectra the absorption bands observed in the range of 541-563 cm^{-1} and 421-461 cm^{-1} are attributed to the fusion of Gr in *MMZB Ferrite/Gr Composites*. The d.c resistivity of ferrite samples increased as the temperature increased in ferromagnetic region up to curie temperature, after that its decreased. However, increase in resistivity was observed with increasing Gr concentration except at Gr = 3%. The values of optical band gap were found to decreased from 4.45 to 3.50 eV with increasing Gr content. It has been observed that both the dielectric constant and loss factor decreased with the increase of frequency. The minimum dielectric loss was observed for Gr =4 %. The values of saturation magnetization and microwave frequency decreases with fusion of Gr. A remarkable change in microstructures, electrical and magnetic properties was observed with fusion of Gr. Due to these promising properties these materials may be used for microwave frequency devices.

KEYWORDS: ferrites; graphene; Composites; Sol-gel auto combustion; dielectric

1. INTRODUCTION

Nano scale polycrystalline ferrites with one of a kind electrical and magnetic properties are of incredible awareness for researcher and engineers. Significantly after the greater part of the century the researcher, scientists and engineers are as yet energized in different sorts of nanocrystalline materials. Transition metal oxides (MFe_2O_4) with cubic spinel structure, have utilized in different electronic and electrical applications for the most recent decade [1]. Ferrites contribute a fundamental role in a numerous potential application because at room temperature, their high DC electrical resistivity and low electrical misfortunes over expansive range of frequencies. Analysts offer inclination to spinel ferrites in light of the fact that of sensible cost, mechanical hardness, compound steadiness at high temperature and high DC resistivity [1]. Ferrites physical properties have great dependence to the cation distribution among the tetrahedral (A) and the octahedral (B) sites in the lattice. Dependent on the assumption of the different cation substituents over tetrahedral and octahedral sites, its attractive and electrical properties can be adjusted rendering to research interest. Spinel ferrites have broad potential applications in variety of fields including microwave and switching devices [2]. These properties can be enhanced by presenting some rare earth particles into the interstitial sites. It is accounted for by numerous specialists that the ferrites substituted with rare earth components cause the change in structural what's more, the magnetic properties [3]. Ferrites are very operative as microwave protections because of their low cost, high resistivity loses and small eddy loss. The small number of nonmagnetic ions results in the modification of saturation magnetization. The impact of Al doping on the structural and electrical properties of Ni–Cd ferrite have been studies. The effect of praseodymium on structural and magnetic properties of Cobalt-Zinc spinel ferrites have been studied [4]. Gr has two-dimensional structure du to which it has wide range of applications in microwave absorption and electronics. Further fusion of Gr with ferrite improves the properties of Gr\ferrite composites and make them very promising material for microwave absorbing devices.

In present case we have Study the effect of Gr on structural and electrical properties of composites of $Mg_{0.5}Mn_{0.375}Zn_{0.125}Bi_{0.05}Fe_{1.95}O_4$ ferrite and Gr (***MMZB Ferrite/Gr Composites)*** by changing the Gr percentage as (Gr= 0%, 1%, 2%, 3%, 4%) via sol gel method.

2. EXPERIMENTAL METHOD

Preparation of ***MMZB Ferrite/Gr Composites*** ($Mg_{0.5}Mn_{0.375}Zn_{0.125}Bi_{0.05}Fe_{1.95}O_4$ and Gr***)*** by changing the Gr percentage as (Gr= 0%, 1%, 2%, 3%, 4%) were carry through sol gel auto combustion method. The starting materials, for sol-gel auto combustion method, proportion were

$Mg(No_3)_2$.$6H_2O$ (Magnesium nitrate), $Mn(No_3)_2$. $4H_2O$ (Manganese nitrate), Bi $(No_3)_2$. $5H_2O$ (bismuth nitrate), Zn $(No_3)_2$. $6H_2O$ (Zinc nitrate), Fe $(No_3)_3$. $9H_2O$ (Iron nitrate) and Graphene. Citric acid and nitrates\Gr were dissolved in distilled water with 1:1 molar ratio at room temperature. With the help of ammonia pH of the solution were adjusted at 7. For proper mixing the temperature of hot plate kept 373 K. Then the solution was permitted to evaporate and transform in to gel on heating at 750 K. This further heating allows the gel to burn in a self-ignition manner and form the fluffy loose powder on complete combustion followed by heating at 833 K for 4 h to remove organic materials. With the help of the agate mortar and pestle the prepared sample was grinding for a long time until nano particles were formed. When grinding has been done all the samples were put in to the crucible of 25ml and put the crucible in to the furnace simultaneously for 6 hours at 1073 K. Aftert the sintering, the powder is again evaluating to until it become a delicate powder. The sintered powders were then pelletized in circular disks of 7 mm diameter by applying a uniaxial load of 1500 ton.

These composites further characterized for the electrical properties by using two-probe method within the temperature range of 373 K to 873 K. The dielectric properties have been studied at room temperature as a function of frequency in range of 8Hz to 8MHz.

3. RESULTS AND DISCUSSION

3.1 Structural analysis

The X-ray diffraction pattern of prepared nano-ferrite samples with nominal composition ***MMZB Ferrite/Gr Composites*** are shown in Fig 1. By using Bragg's law All the peaks were indexed. XRD pattern of the samples have displayed the peaks at reflection planes (2 0 0), (3 1 1), (4 0 0), (4 2 2) and (511). All the peaks indicate the presence of crystalline single phase with cubic spinel structure [5]. The X-ray diffraction peaks was used to calculate the crystallite size using the Debye–Scherrer Equation. All diffraction peaks representing advanced degree of crystallinity with well-defined peaks.

$$D=\frac{K\lambda}{\beta cos\theta} \quad \text{-------------------------(1)}$$

where λ is the radiation wavelength and full width at half maximum (in radians) is β at 2θ position and D is the crystallite size. K is a dimensionless shape factor having value 0.9. The average crystalline size of the samples was seen as in the range 22.26-22.97 nm (c. Table 1). The graph between crystallite size and Gr concentration are shown in Fig 2.

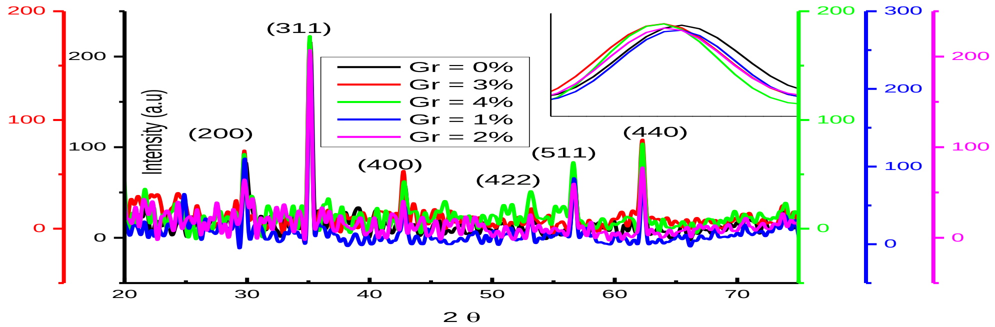

Fig. 1 ***XRD comparative intensity plot for MMZB Ferrite/Gr Composites***

For the calculation of the lattice parameter of the sample's following equation is used.

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}} \quad \text{----------------------- (2)}$$

Where hkl is miller indices, d is interplanar spaces and "a" is lattice constant. By using XRD information lattice parameters, lattice constant, volume of the unit cell and X-ray density of samples are detected and presented in Table 1. With the increase in Gr concentration, there is a variation in lattice parameters as clear from Table 1. The graph between lattice parameter and Gr concentration is shown in Fig 2.

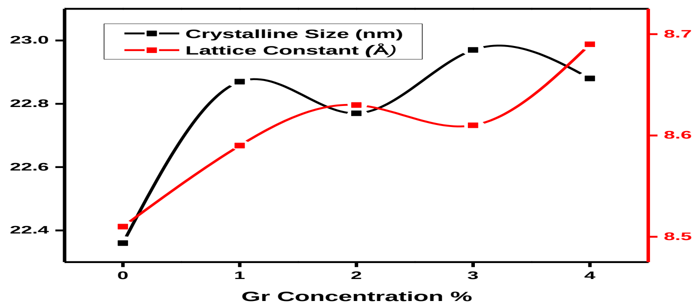

Fig 2. ***Plot of crystalline size and lattice constant verses GR concentration of MMZB Ferrite/Gr Composites***

Table 1: ***Crystallite size (D) Lattice constant (a), Volume of unit cell and X-ray density of MMZB Ferrite/Gr Composites annealed at 1073 K.***

Graphene Percentage	average Crystalline Size(nm)	Lattice Constant a (A°)	Volume of the unit cell V	Xray density g/cm^3
0 %	22.36	8.51	616.30	5.30
1 %	22.87	8.59	633.84	5.35
2 %	22.77	8.63	642.73	5.48
3 %	22.97	8.61	638.28	5.41
4 %	22.88	8.69	656.23	5.53

The X-ray diffraction patterns of as-prepared samples confirmed the formation of single-phase cubic spinel structure.

3.2 FT-IR

The FT-IR Spectra of ***MMZB Ferrite/Gr Composites*** are shown in Fig 3. In general, the FT-IR analysis was taken from 2000 to 400 cm^{-1} for ferrite \composites. The absorption bands in the range of 400–1000 cm^{-1} corresponds to the stretching vibration of tetrahedral and octahedral sites [6]. The FTIR bends show numerous peaks. The wave quantities of peaks are classified in the table 2.

Table 2: ***FTIR peaks for series MMZB Ferrite/Gr Composites***

Gr Concentration (%)	ν_2 (cm^{-1})	ν_1(cm^{-1})
0	461	545
1	454	541
2	421	563
3	423	547
4	422	561

The low frequency band ν_2(421-461 cm^{-1}) and high frequency band ν_1 (541-563 cm^{-1}) are measured to the tetrahedral and octahedral sites commonly in a spinel construction. For the formation of ferrite (spinal structure) material these two bands are responsible. So, the band (545cm^{-1},541cm^{-1},563cm^{-1},547cm^{-1},561cm^{-1}) which are related to the stretching vibrations of tetrahedral metal oxygen bond which is related to higher frequency absorption band. The band (461cm^{-1},454cm^{-1},421cm^{-1},422cm^{-1}) which are related to the stretching vibrations of octahedral sites, and it is related to the lower frequency band [7].

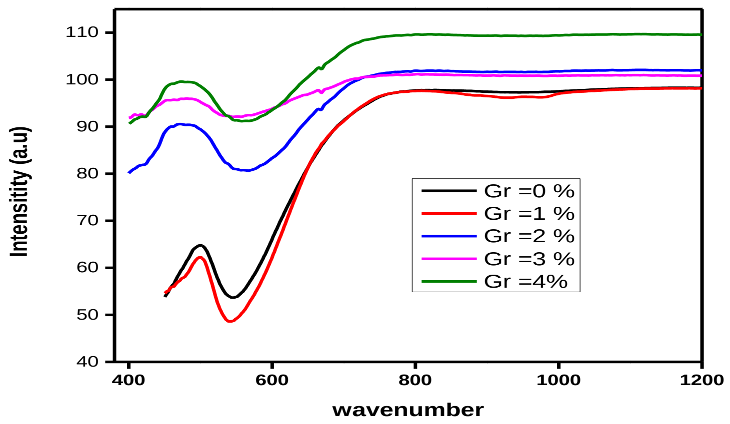

Fig 3. ***FTIR Curves for MMZB Ferrite/Gr Composites***

The region from400 cm^{-1} up to 1600 cm^{-1} is called finger print region, it is due to stretching and binding vibrations.

3.3 I-V Analysis

The electrical properties (Dc resistivity) of all the prepared ***MMZB Ferrite/Gr Composites*** sintered at 1073 K are assessed through two probe method. The resistance of fabricated samples is determined by slope of I-V plot, where voltage and current were along x-axis and y-axis respectively. The temperature is kept in the range 373 – 733 K. The DC resistivity ($\rho = \frac{RA}{h}$) of all samples was evaluated with resistance ($R = \frac{1}{slpoe}$) offered by pellets, Where h

corresponds to thickness of pellets and *A represent* area of cross section of pellets. The DC resistivity of all fabricated nano ferrites are calculated by using two probe method in the temperature range from 350 K to 700 K. Silver paste are used to make good electrical contact between surface of pellets and electrodes. The electrical resistance is calculated by taking inverse of slope from current-voltage plot, where voltage was along x-axis and current was along y-axis.

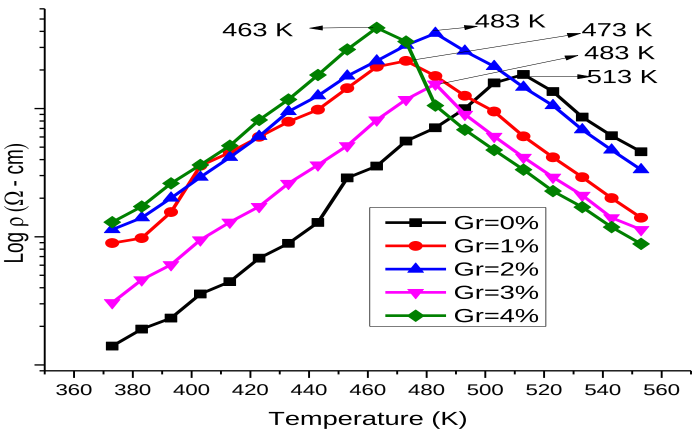

Fig 4 ***Variation of resistivity with temperature of MMZB Ferrite/Gr Composites***

The electrical resistivity (DC) of ***MMZB Ferrite/Gr Composites*** has been measured with respect to temperatures (350-700 K) as appeared in Fig 4. The resistivity increased as temperature increase that shows the ferromagnetic nature of prepared nano powder. Change in resistivity as a function of concentration is also computed as shown in Fig 5. Fig 5 (a) represents the trend of resistivity at low temperature. At low temperature before curie temperature i.e ferromagnetic region it was observed that resistivity had minimum value for Gr =0 % and maximum for Gr= 4 %. In 2nd region Fig 5 (b) represents the variation of resistivity in transition region, when the materials convert ferro to paramagnetic. Fig 5 (c) reflects the variation of resistivity in par region. In para region i.e at high temperature it was observed that the resistivity has maximum value at Gr =0 % and minimum at Gr = 4 %. In spinel ferrites conduction occurs due to exchange between similar ions have different valence state. In particular, the conduction is attributed to the hoping of electrons between Fe^{3+} and Fe^{2+} at crystallographic sites [8]. The resistivity of all sample decreased as temperature increased after the curie temperature that is because of increase in hoping of charge carriers.

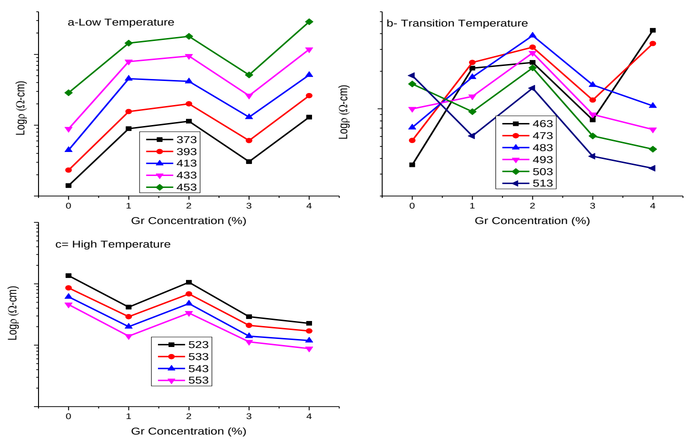

Fig 5 ***Graph between Gr concentration (x) versus log of resistivity of MMZB Ferrite/Gr Composites at a) Low temperature b) Transition temperature c) High temperature.***

This may be due to increase in n-type hoping conduction of Fe^{2+}-Fe^{3+} ions. Fig. 6 represents the Arrhenius plots of the ***MMZB Ferrite/Gr Composites.*** The slope of the plots was used to calculate the activation energy of the para and ferro region of the composites. The net activation energies are 0.63, 0.75, 0.83, 0.79 and 0. 735 for Gr 0% , Gr 1%, Gr 2% , Gr 3% and Gr 4% respectively.

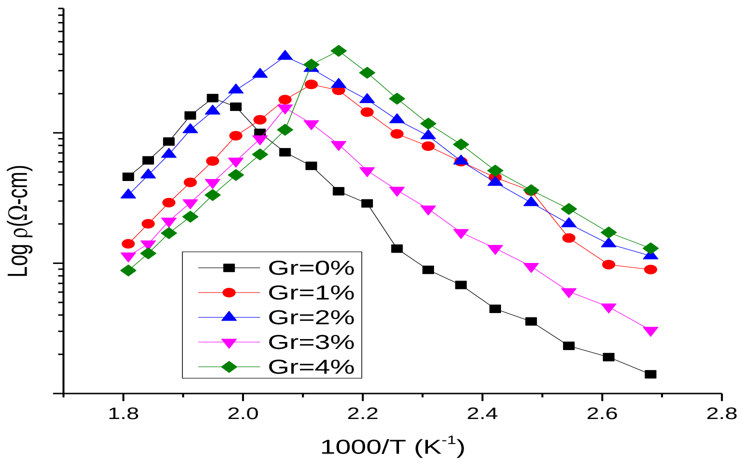

Fig 6 ***Variation of resistivity with 1000/temperature of MMZB Ferrite/Gr Composites***

3.4 Optical Band gap

The energy band gap of the prepared ***MMZB Ferrite/Gr Composites*** are calculated with UV visible spectrometer as shown in Fig 7. The energy band gap (Eg) of the nanocomposites is calculated from the fundamental absorption, that is corresponding to the electron excitation from the valence to the conduction band (Kiran, V. S et al 2017). The optical band gap is calculated from the equation ($\alpha = \frac{A\,(h\nu - E_g)^{1/2}}{h\nu}$). In the equation h is plank's constant, α is absorption coefficient, ν is the frequency of light, A is known as proportionality constant and Eg stands for energy band gap. The energy band-gap is computed through plotting the graph amongst $(\alpha\nu h)^2$ versus (hν).

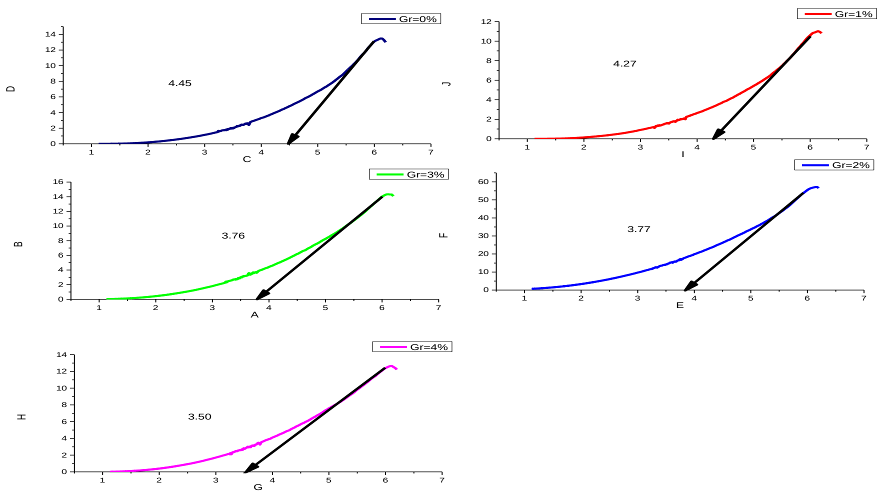

Fig 7. ***Band gap energy for MMZB Ferrite/Gr Composites***

For the calculation of absorption coefficient α the fundamental relations used are: I= $I_o\, e^{-\alpha t}$, A = log (I / I_o) and $\alpha = 2.303\,(A/t)$. In the equation "t" stands for the thickness of the sample and "A" is the absorbance [9]. The energy band gap value for all the samples has been found in the range of 4.45 - 3.50 eV. The band gap of mixtures is decreases with Gr concentration. The band gap values of Gr functionalized with MMZB ferrite are summarized in table 3.

Table 3: ***Energy band gap and resistivity of prepared MMZB Ferrite/Gr Composites***

Gr-Concentration (%)	Band gap (ev)	Resistivity x 10^7 (Ω-cm)
0	4.45	0.14
1	4.27	0.89
2	3.77	1.13

3	3.76	3.06
4	3.50	1.30

4.5 Dielectric study

The fabricated material having composition ***MMZB Ferrite/Gr Composites*** is analyzed in the frequency range of 8Hz to 8MHz for dielectric study and variation of dielectric constant vs frequency is shown in the Fig 8.

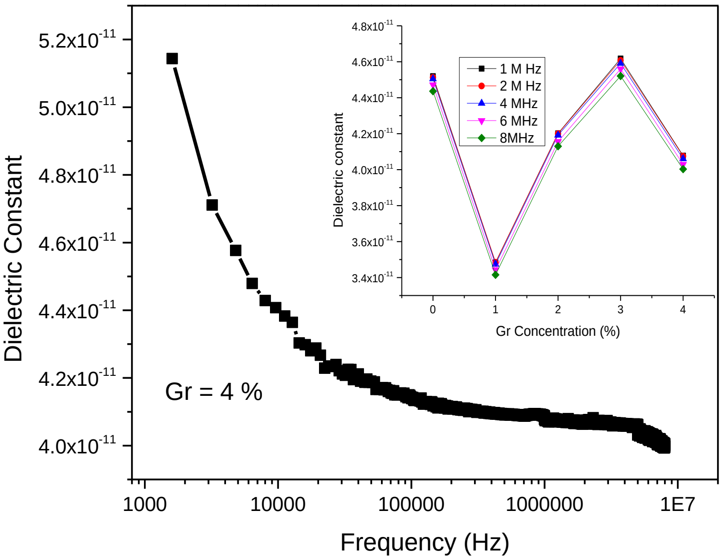

Fig 8. Graph between log of frequency vs dielectric constant of *MMZB Ferrite/Gr Composites.* The inset represents the variation of dielectric constant with Gr concentration.

It is noted from the Fig. 8 that all the manufactured samples have reducing tendency with rise in the frequency range. It is noted that at lower frequency values the dielectric constant has higher values but with the growth in the frequency values there is a sudden decrease in the dielectric constant, which may be attributed to the fact that, the permanent dipoles adjust themselves along the field direction at low frequency and at higher frequency values the polarization process is reduced [10]. Also, the variation in the field is just excessively fast at a higher frequency for the dipoles adjust themselves along the direction of the field. In this way, with the growth in frequency the dielectric constant decreased. Inset of Fig. 8 shows, the variation in dielectric constant with Gr concentration at various frequencies. So in the present study it is noted that by fusion of Gr in the composites, the space charge polarization process occur and hence dielectric constant is decreased.

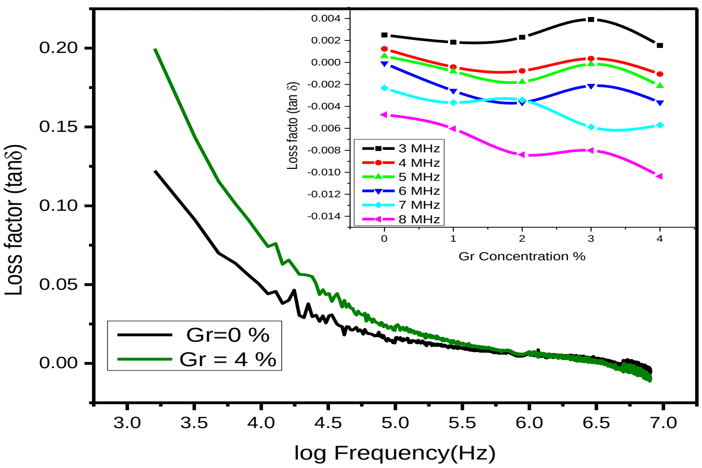

Fig 9. Graph between log of frequency vs tangent loss of *MMZB Ferrite/Gr Composites*

It is noted from the above Fig. 9 that value of dielectric loss is decreasing as, growing the frequency values and at certain frequency limit the dielectric loss almost becomes constant. In the presence of AC field, dielectric loss is basically the electrical energy lost in the form of heat. At lower frequency values the value of dielectric loss is higher because of the fact that at lower frequency values there is a high resistance in polarization process and at lower frequency values the values of resistivity are low in polarization process. At a certain value of frequency, the dielectric loss becomes almost independent of the frequency [11]. Inset of Fig 9 represents the variation of So, in the present study it is noted that by addition of cadmium ions in the sample the space charge polarization process and hence dielectric constant and dielectric losses are decreased. The dielectric constant and loss factor (tan δ) were exhibiting normal behavior as a function of applied frequency.

4.6 VSM Analysis

The hysteresis loops of ***MMZB Ferrite/Gr Composites*** were shown in Fig 10. The saturation magnetization lied between the soft magnetic materials. Different parameters like saturation magnetization (M_s), remanent magnetization (Mr), and coercivity were determined from these loops and presented in Table 4.

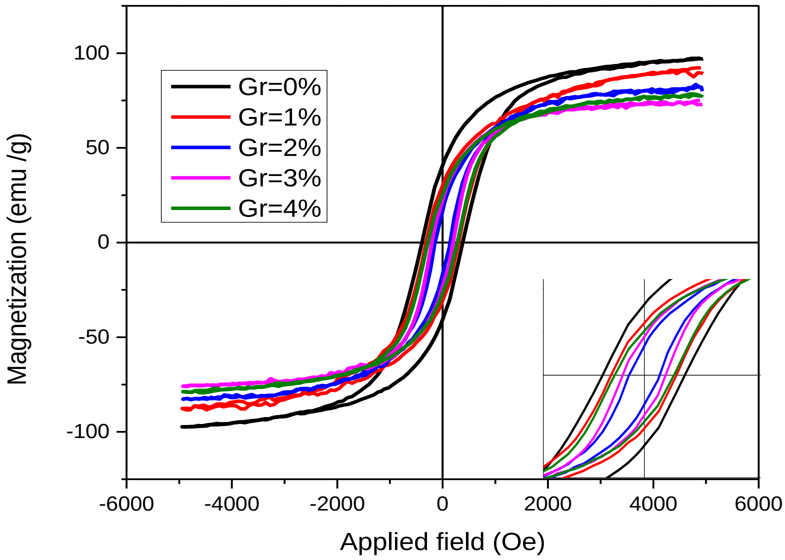

Fig 10. ***M-H loops of MMZB Ferrite/Gr Composites***

The value of saturation magnetization of the ***MMZB Ferrite/Gr Composites*** reduces significantly with addition of Gr. Mr and Hc has the minimum value for 2% Gr composites and maximum for the 0% Gr concentration. The squareness ratio (SQ = Mr/Ms) are the important parameter for recording media application. The minimum value of SQ was observed for 2% Gr and Maximum for 0% Gr. The value of magnetization lowered due to the formation of antimagnetic composites with addition of Gr. When the external field applied on these composites, this field arrange the domains in the direction of field and removing the field the residual magnetization remains due to magnetic domain walls. With the addition of Gr the restriction of these wall reduces and minimum value of Mr was observed for Gr 2%. The microwave frequency $\omega_m = 8\pi$ Ms γ (where γ = 2.8 MHz/Oe is a gyromagnetic fraction) was determined

Table 4: ***Magnetic parameters of MMZB ferrite/Gr Composites***

Gr %	M_S (emu/g)	Mr (emu/g)	H_C (Oe)	S.Q = Mr/Ms	ωm (GHz)
0	97.77	41.00	379.13	0.42	21.63
1	90.38	29.67	300.12	0.33	20.00
2	82.35	16.54	142.09	0.20	18.22
3	78.08	22.05	196.79	0.28	17.27
4	73.32	25.43	275.80	0.35	16.22

SUMMARY

In the present work Gr functionalized with MMZB Ferrite were synthesized by sol gel auto combustion method. The prepared nanocomposites were confirmed by XRD, FTIR, IV measurement and UV-vis. XRD analysis shows the formation of single-phase cubic spinel structure. The value of lattice constant lies in the range of 8.51 Å to 8.69 Å. The average crystallite size of as-prepared composites is found in the range of 22.36 to 22.96 nm. The FTIR bends show the stretching in tetrahedral and octahedral sites in a spinel structure due to Gr. Electrical properties had numerous effects with fusion of Gr in MMZB Ferrite/Gr Composites. At low temperature the resistivity has maximum value for Gr = 4 % while for high temperature its maximum for Gr = 0%. It was observed that the resistivity increases in ferro region and decreases in para region with increase of temperature. It was also observed that with the addition of Gr concentration the values of energy band gap decreased. Dielectric behavior shows that at low frequency there is sudden decrease in dielectric constant and dielectric losses. The Saturation magnetization (Ms = 73.22 emu/g) and microwave frequency (16.22 GHz) has minimum values for Gr = 4%. While Hc, Mr and S.Q are minimum for Gr = 2%. All these whimsical properties indicates that these composites may be used for microwave devices.

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