Tailoring of Structural, electrical, and dielectric properties of Mg-Mn-Bi nanoferrites with addition of Zn

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Zin substituted Mg-Mn-Bi nano ferrites, $Mg_{0.5}\,Mn_{0.5-x}\;Zn_x\;Bi_{0.05}Fe_{1.95}O_4$ (x= 0, 0.125, 0.25, 0.375, 0.5) were synthesized using the sol gel auto combustion method. Structural parameters were analyzed through x-ray diffraction. It was revealed that all the samples are single phase spinel structure with Fd-3m space group and crystallite size, lattice constant and x-ray densities were varying with Zn concentration. RAMAN analysis showed the cation vibration. The DC resistivity was enhanced of all the samples with increasing concentration of Zn. The substitution of Zn also responsible for the variation of magnetic parameters as observed with VSM. Due to these remarkable properties all the prepared samples may be utilized at high frequency in microwave devices.

Keywords: crystallites size; magnetic; electric; dielctric.

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1. Introduction

Nano scale polycrystalline ferrites with one of a kind electrical and magnetic properties are of incredible awareness for researcher and engineers. In the past two decades, nano materials have become a very stimulating research subject and increasing day by day [1]. Just a while ago, Rare earth substituted magnetic nano-material have been explore for various applications like moisture and gas sensor. Depending upon the nature and quantity of rare earth element, electrical, magnetic and structural properties of ferrites modify by adding up of minute quantity of rare earth ions to ferrite specimen. [2] [3]. Ferrites are chemical compounds having general formula AB_2O_4, in which A and B correspond to different metallic cations and generally include iron. Like other ceramic materials, ferrites are hard and brittle. Due to their magnetic properties, ferrites are generally classified into soft and hard. Metals like Zinc, Manganese or Nickel are called soft ferrites due to having small coercivity. In distinguish, magnetic materials made up of iron oxide and strontium or barium oxides are called hard ferrites (or permanent magnets)[4]

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In normal spinel ferrites, all bivalent metal ions occupy tetrahedral [A] sites & trivalent [B] ions occupy octahedral sites. Chemical formula of these types of ferrites is M^{2+} $[Fe_2^{3+}]$ O_4^{2-}. Magnesium ferrites Mg^{2+} $[Fe^{2+}Fe^{3+}]$ O_4^{2-} belong to this category. Whereas in inverse spinel ferrite all divalent ions $[A^{2+}]$ occupy octahedral sites while trivalent ions $[B^{3+}]$ are equally distributed between A and B site [5]. The chemical formula of such ferrites is Fe^{3+} $[M^{2+}Fe^{3+}]$ O_4^{2-}. [6]. Spinel ferrites are used in various devices like high bulk magnetic storage, switching circuits, telecommunication tools, microwave based instruments, gas sensors and magnetic fluids etc. [7]. At low temperature ferrites are insulators and at moderately high temperature these are semiconductors. The improvement in dielectric properties make them favourable candidate for microwave and hig frequency applications. These properties such as magnetic, electrical and structural can be conroleld with the synthesis methods. Various techniques could be used for synthesis of these magnetic nanoparticles like sol gel, hydrothermal, micro-emulsion and co-precipitation method. [8] In this study we investigate the improvement in structural, electrical and magnetic properties in Mg-Mn-Bi nano ferrites, ($Mg_{0.5}\,Mn_{0.5-x}\,Zn_x\,Bi_{0.05}Fe_{1.95}O_4$ (x= 0, 0.125, 0.25, 0.375, 0.5)) with the doping of Zinc (Zn doped MMB-nanoferrites).

2. Materials and methods

For the preparation and synthesis of Zn doped MMB-nanoferrites sol-gel auto combustion method was used. The required metal nitrates $Mg(NO_3)_2.6H_2O$, $Mn(NO_3)_2.6H_2O$, $Zn(NO_3)_2.xH_2O$ $Bi(NO_3)_3.6H2O$ and $Fe(NO_3)_3.9H_2O$ according to the stochiometric ratio were dissolved in distilled water. Stoichiometric amount of nitrates of Mg, Mn, Zn, Fe, Bi and citric acid were taken according to calculation. The above-mentioned nitrates in addition to citric acid were mixed in ionized water and stimulated. Then magnetic stirring was used and ammonia solution (NH_3) was added drop by drop continuously to attain Ph. 7 during stirring. Then the solution was heated on hot plate magnetic stirrer till the gel is form. After continuously heating, rapid combustion of gel causes its complete burning to form ash product. Samples product annealed for 2 hours at temperature 500 °C. To attain fine powder product, samples were again grind for 1-2 hour, after that the specimens was placed in furnace for sintering for 8 hours at 750°C and grinding. Then samples ready for characterized by using different techniques.

2.1 Characterization techniques

For structural and morphological studies, we have used powder X-Ray diffraction, XRD (using D8 advance Bruker diffractometer with Cu-Ka radiation, λ = 1.5406 A°), FT-IR spectroscopy (using Bruker Tensor II) and scanning electron microscope, SEM characterization techniques were employed. For DC resistivity measurement we used current voltage measurement (I-V).

3. Result and Discussion

3.1. X-Ray Diffraction Analysis

Crystalline Structure and formation of spinel structure has been investigated by XRD. Figures Showed the XRD pattern of synthesized nanoparticles that contain the Zn doped MMB- spinel ferrite

which synthesized by sol-gel auto combustion method. The different peaks with planes (220), (311), (400), (511) confirm the formation of single phase with Fd-3m space group of all spinel ferrite. The crystallite size of peak (311) was calculated by using the Debye–Scherrer Equation. All diffraction peaks represent advanced degree of crystallinity with well-defined peaks. From Table 1 the crystallite size was decreased with the addition of Zn in MMB ferrites. To calculate the dislocation density (δ) the following formula was used [9];

$$\delta = 1/D^2 \quad (1)$$

It was observed that the dislocation density was increased with the addition of Zn from 4.06×10^{-4} nm^{-2} to 6.46×10^{-4} nm^{-2}, as presented in Table 1. The Braggs equation was used to determine the interplanar distance (*d*), that is given below [10-13];

$$2dsin\theta = n\lambda \quad (2)$$

where *n* represents the order of reflection. The lattice constant (*a*) was assessed using equation [14-16];

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (3)$$

Here, *h k l* are the miller indices of the planes. The volume of the unit cell (*V*) was anticipated *via* the below equation [17];

$$V_{cell} = a^3 \quad (4)$$

The variation in the lattice constant, interplanar distance, and unit cell volume were observed with increasing the Zn percentage as clear form Table 1. The variation in lattice parameters may be due to the fusion of Zn in the MMB ferrites lattice.

Table 1. Structural parameters of Zn doped MMB-nanoferrites

Composition (x)	**2θ (degree)**	**h k l**	**FWHM**	**D (nm)**	**δ × 10^{-4} (nm^{-2})**	**a (Å)**	**V ($Å^3$)**
0	35.28	311	0.173	49.52	4.07	8.42	598.07
0.125	35.95	311	0.177	48.73	4.21	8.41	596.41
0.25	35.41	311	0.190	45.07	4.92	8.43	599.61
0.375	35.51	311	0.218	40.72	6.03	8.44	600.67
0.5	35.86	311	0.274	39.33	6.46	8.40	590.38

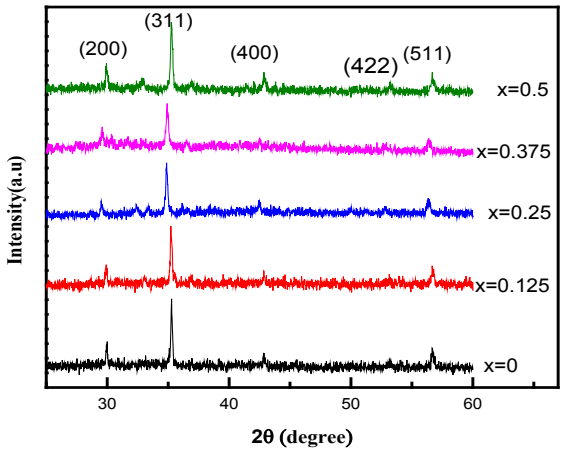

Fig. 1. XRD spectra of Zn doped MMB-nanoferrites

3.2 Raman analysis

Fig. 2 represents the Raman spectra in the range of 0 – 1000 cm^{-1} of *Zn doped MMB-nanoferrites.* The variation in vibrational bonds due to Zn concentrations is shown in Table 2. The vibration modes E_g, $3T_{2g}$, $2T_{2g}$, fit for octahedral site and A_{1g}, *and* $1T_{2g}$ belong to tetrahedral site [18-20]. The strong disparity in vibrational bond related to tetra site confirms the replacement of Zn on Mn. A variation on octa site is due to the movement of oxygen atoms when Mn is replaced by Zn.

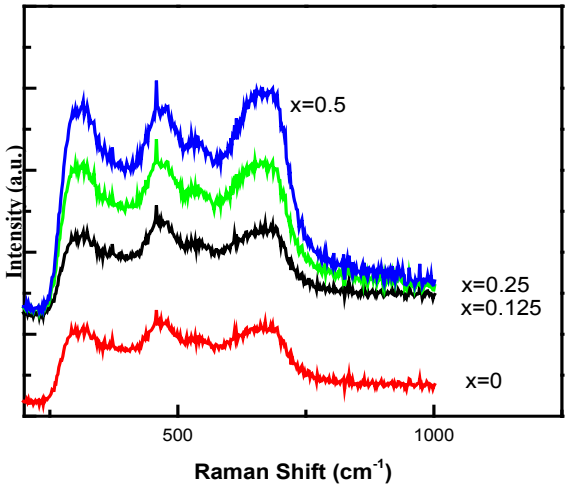

Fig. 2 Raman spectra of Zn doped MMB-nanoferrites

Table 2. Raman modes of Zn doped MMB-nanoferrites

Samples (x)	**T_{2g} (1)**	**E_g**	**T_{2g} (2)**	**T_{2g} (3)**	**A_{1g}**
0	310	375	473	535	671
0.125	326	362	465	542	668
0.25	313	351	475	551	666
0.5	321	348	469	543	677

3.4 Electrical analysis

DC resistivity of Zn doped MMB ferrites was conducting using a two-prob technique in the temperature range of 373-413 K. The DC resistivity for each sample was calculated from the resistance and dimensions of pallets using the formula [21];

$$\rho = RA/L \tag{5}$$

where R is the resistance of pellets, A is the cross-sectional area and L is thickness of pellet. The variation of resistivity with Zn at different temperatures is presented in Fig. 3. The replacement of Zn on Mn reduced the resistivity of all the prepared samples. The decreased in resistivity is due to the conductive nature of Zn.

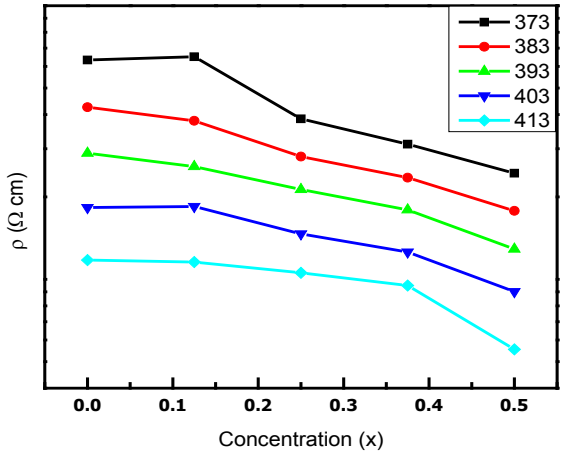

Fig. 3 Zin concentration (x) versus resistivity of Zn doped MMB-nanoferrites

3.5 Dielectric analysis

The discrepancy in dielectric constant versus Zn concentration of *Zn doped MMB-nanoferrites* was described in fig 4. It was noted that the dielectric losses has minimum values for X =0.125 for all frequencies. It was also observed the dielectric losses were increases with the increase of frequency. The variation of dielectric losses with Zn concentration and frequency may be due to electron hopping at grain boundaries. This variation may be explained by using the Koops and Maxwell-Wagner model [22].

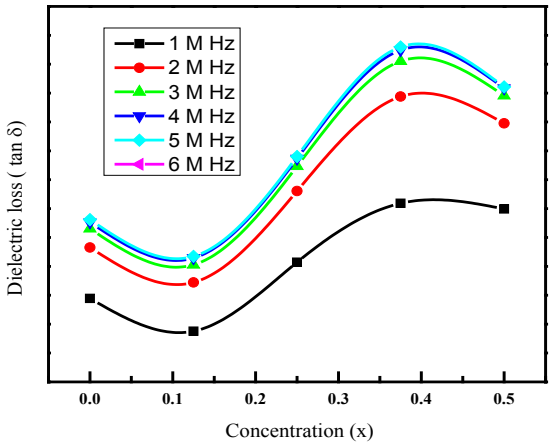

Fig. 4. Zin Concentration (x) versus dielectric loss of Zn doped MMB-nanoferrites

3.6 Magnetic analysis

The magnetic parameters of Zin doped MMB-nano ferrites were calculated from hysteresis loops. Hysteresis loops of all the samples were presented in Fig. 5. The saturation magnetization (Ms),the remanence, coercivity, The squareness ratio (SQ = Mr/Ms) and magneto crystalline anisotropic constant ($K = \frac{Hc \times Ms}{0.96}$) were determined and presented in table 3. The maximum saturation magnetization (Ms) was observed for x=0.125 having value 118.88 emu/g. For all other samples the magnetization decreased with the addition of Zn. As Zn is paramagnetic material due to this the saturation magnetization decreased with addition of Zn [20]. The higher value of magnetization for x=0.125 is due to strong super exchange Heisenberg interactions in ferrites. Neel's sub-lattice theory can be used the interaction of magnetic ions in Zn dopped MMB-ferrites [20-21]. The remanence and SQ were minimum for x=0.375 concentration of Zn. The crystalline anisotropy constant for Zn doped MMB-nanoferrites was also reduced with the addition of Zn in MMB-nanoferrites sample. The minimum magneto crystalline anisotropic constant was observed for Zn 0.5 concentration.

Table 3. Magnetic parameters of Zn doped MMB-nanoferrites

Samples (Concentration X)	**M_S (emu/g)**	**M_R (emu/g)**	**H_C (Oe)**	**SQ**	**K (erg/cm^3)**
0	95.31	54.88	492.14	0.57	48860.27
0.125	118.88	49.45	253.97	0.42	31449.95
0.25	103.26	48.74	395.59	0.47	42550.65
0.375	91.76	12.15	30.17	0.13	2883.75
0.5	83.15	13.09	25.88	0.16	2241.58

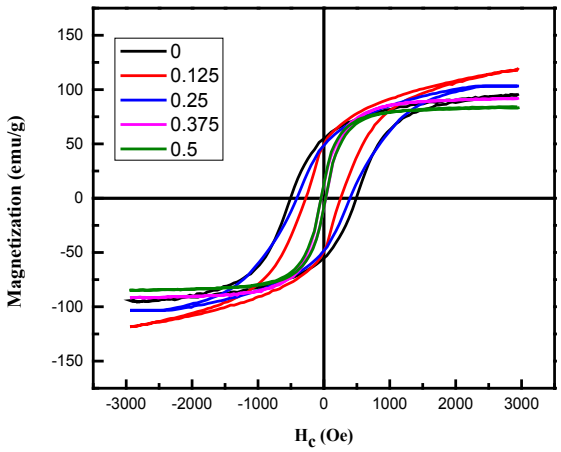

Fig. 5. M-H loops of Zn doped MMB-nanoferrites

5. Conclusion

Zin doped MMB-nanoferrites were prepared *via* sol gel auto combustion process and their structure was studied by using XRD and Raman analysis. The structural parameters increased with the incorporation of Zn. However, minimum resistivity was observed for Zin concentration 0.25. The dielectric loss tangent (tan δ) had minimum value for Zn concentration 0.125 for all frequencies. Maximum saturation magnetization was observed for x= 0.125 and minimum coercivity was observed for x=0.5. Therefore, this material may be utilized for high frequency applications.

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