Frequency Dependence Dielectric Behaviour of Polycrystalline Mn Substituted Zn Nanoferrites by Sol-Gel Route.

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Abstract:

Dielectric properties of Mn-Zn nanoferrites such as dielectric constant(□'),dielectric loss(□") tangent and conductivity has been investigated in the frequency range 100Hz to 10MHz the variation in the above parameters of dielectric properties with frequency and temperature is explained qualitatively. The dielectric constant $Mn_{0.5}Zn_{0.5}Fe_2O_4$ is found to be less than the bulk sample.the migration of Fe^{3+} ion from octahedral site to tetrahedral site decreases the dielectric constant with increase in Mn consentration.The charge libration of charge and electron hopping mechanism can be explained together for the conduction mechanism in present compound . The formation of spinel structure and grain size was confirmed using X-ray diffraction technique and transmission electron microscopy (TEM) which confirmed by scaning electron microscopy (SEM).

Keyword: Chemical synthesis, MZN, X-ray diffraction, Dielectric properties.

1. Introduction

Magnetic properties of magnese substituted zinc nanoferrites exhibits superparamagnetic behaviour which is most useful in medical field such as MRI, bioseperation and magnetic senser [1-4] etc. Similarly the dielectric properties of such material playing important role in microwave devices such as isolators circulators, transformer, electric generators storage devices etc [5]. The dielectric properties of ferrites are dependent upon several factors including the method of preparation,chemical composition and grain structure or size, also it is Mn-Zn ferrites have attracted a great deal of interest and are chosen for the present work to deal with the dielectric properties as a function of frequency and temperature was taken.when a ferrite is sintered under slightly reducing condition the valence state changes. The individual cation formed in the sample leads to high conductivity and when such a material is cooled in an oxygen atmosphere, it is possible to form films of high resistivity over the constituents' grains. Such a ferrite in which the individual grains are separated by either air gap or low conducting layers behaves as in homogeneous dielectric materials. Many involved in the low frequency dielectric behaviour of ferrites the prominent ones are koops [6], Iwachi et.al [7] Koops [6] gave a phenomenological theory of dispersion based on the Maxwell-Wagner interfacial polarization model for inhomogeneous dielectric structure. It was assumed that the solid consists of well conducting grain separated by poorly conducting layers this model explain a strong dispersion in dielectric constant □' and dielectric loss □"at low frequency. Thus, Dielectric constant of polycrystalline ferrites is related to the grain size of the sample in the composition. The frequency dispersion studies suggest that the grain of different sizes contribute differently to the value of dielectric constant and its relaxation frequency.

2. Experimental Details

Powder of magnese zinc nanoferrites having the formula $Mn_{1-x}ZnFe_2O4$ were prepared by sol-gel auto combustion method. Using analytical grade $Mn(NO_3)_26H_2O$, $Zn(NO_3)_26H_2O$ and $Fe(NO_3)_29H_2O$ as starting materials the stoichimetric proportions of above samples were dissolve in deionized water. The mixture of the solution was heated at 80°c on heating plate of magnetic stirrer until the solution transform in to gel was obtained. The gel of the solution which were ignited and burnt in microwave oven 600 watt on 7 min to obtain ash powder of MZF.the powder formed was heated slowly up to 800°c in a furnace for 4 hours after intermediate grinding in pistal morter. the powder formed of the samples were pressed in to circular disc shaped pellets. Silver past coating was done on the surface of the pellets to make the parallel plate capacitor geometry with ferrite material as the dielectric medium.

XRD measurements of the samples were carried out by using Bruker AXE D8 advanced diffractometer with Cu-Kα radiation at room temperature.TEM analysis is done using high resolution transmission electron microscopy (H-7500).The dielectric studies of palletize sample were carried out between the temperature 25°c to 400°c in the frequency range 100Hz to 10MHz using precision impedence analyser Waynkerr 6500B. The dielectric sample is measure using the relation

$\varepsilon' = Cd/\varepsilon_o A$. ---------- (1)

Where 'C' is the capacitance of the sample measured in farad. 'D' thickness of the pallet and A be the flat surface area of pellet and 'ε_o' is the constant of permittivity of free space and its value $\varepsilon_o = 8.854 \times 10^{-12}$ F/m. Dielectric loss is calculated using the relation tanδ=D factor.

The bulk density ρ_m is determined by using the formula

$\rho_m = M/R^2h$------(3)

Where,M is the atomic mass of the sample; 'R' is the radius of the pallet, And 'h' is the height of the sample.

The X-ray density of the prepared sample is calculated by the relation

$\rho_x = 8M/Na^3$----------(4) Where 'M' is mol. Weight of the sample; 'N' is the Avogadro's number (6.63×10^{-23}) a' is lattice constant.

Porosity of the samples calculated by the formula

$P\% = (1-\rho_m/\rho_x)$ ---------- (5) Where, ρ_m is bulk density and ρ_x is x-ray density

Table.1. structural parameter of $Mn_xZn_{1-x}Fe_2O_4$, x =0.5, 1

composition	X-ray Density ρ_x(g/cm³)	Bulk Density ρ_m(g/cm³)	Porosity (p %)	Partical size 'D'(nm)
$Mn_{0.5}Zn_{0.5}Fe_2O_4$,	5.1376	3.1682	38.33%	15nm
$MnFe_2O_4$	5.0430	2.7906	44.66%	16nm

3. Results and discussion

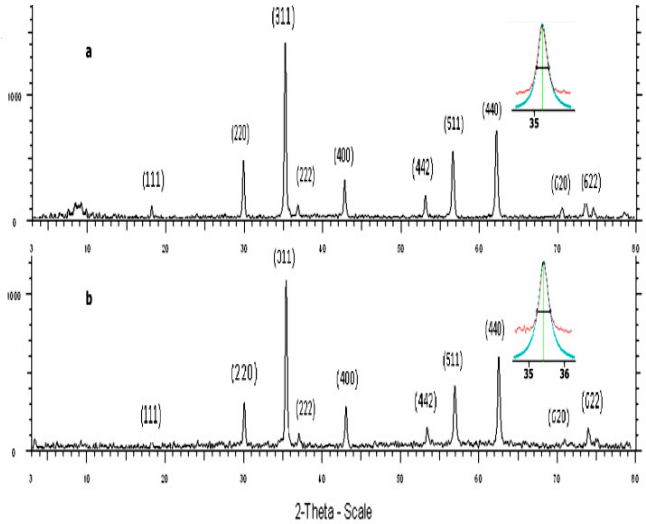

Fig.1. a & b) shows XRD pattern and broading of high intensity peak.

The crystalline structures of MZN were characterized by XRD as shown in above fig.1 (a) & (b). All the Bragg's reflections have been indexed which confirmed the formation of simple cubic spinel structure in single phase without any impurity peak. The strongest reflection and broadening of high intensity peak comes from the (311) planes as depicted by JCPDS card 74-2403. which denote the spinel phase appearing at 35.07^0 & 35.11^0.The crystalline size were calculated for $(Mn_XZn_{1-X}Fe_2O_4$with X = 0.5,1) using high intensity (311) peaks and using Scherer formula i.e. $d_{hkl} = 0.9\lambda/\beta\cos\theta$.The values are found to be 15 nm and 16 nm.The lattice parameter for $Mn_{0.5}Zn_{0.5}Fe_2O_4$ and $MnFe_2O_4$ The values are found to be 8.4812 Å & 8.4699 Å. it was found that the lattice parameter decreases with increasing cations substitution of Mn^{2+} due to difference of ionic radius (ionic radius of Zn^{+2} is 1.35 Å & Mn^{+2} is1.40Å) and its atomic mass.

4. TEM AND SEM Analysis: A typical TEM image of the prepared MZN nanocrystals has been shown in above fig.2

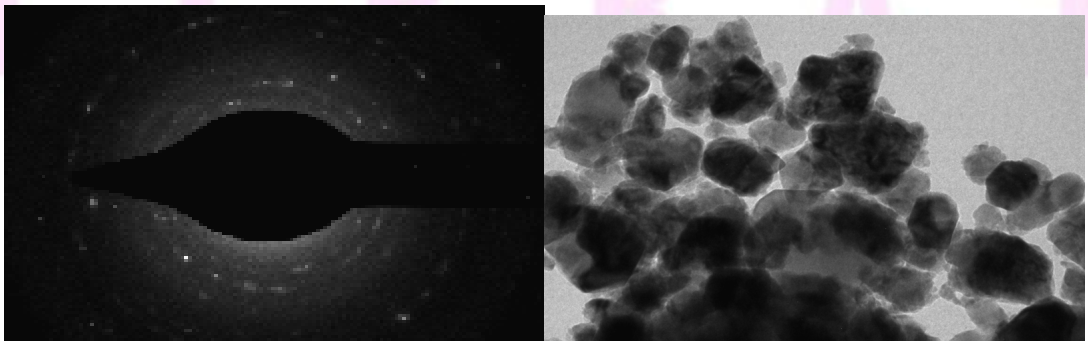

fig.2 A typical TEM image of $Mn_xZn_{1-x}Fe_2O_4$, x =0.5,1 nanoparticles.

The circular diffraction rings are clearly visible, indicating the nano crystalline nature of MZN. Most of the such prepared magnetic nanocrystals are nearly spherical structure as per shown in TEM. Dark regions are representative nanoparticles which are in agreement with the SEM findings below. The morphogical studies of the Mn-Zn ferrite powder was carried out using SEM. This type of electron microscope is capable of producing high resolution images of a sample surface [8-9] due to the manner in which the images are created. SEM images have a characteristic three dimensional appearance and are useful for judging the surface structure of Mn-Zn ferrite. It is found that the powders were made up of particles with the size in the nano range as shown in fig.3.

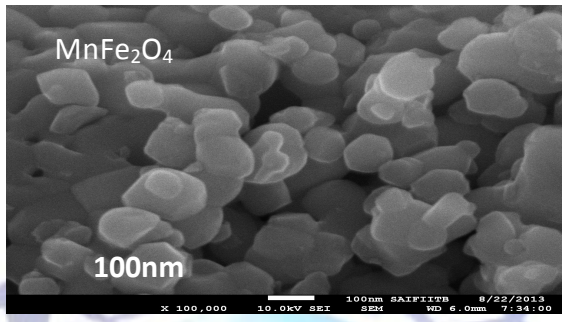

Fig.3.SEM spectrum of the sample$MnFe_2O_4$

In which the powder form of the solid sample was mounted on the conducting resin with dispersion treatment, indicating that the almost spherical and homogeneous nanoparticles with the average size of MZN are about 28 nm. This result is in agreement with the result of XRD and TEM analysis [10].

5. Dielectric Properties

5.1 Dielectric constant: The variation in dielectric constant (□') with frequency at room temperature for the sample $Mn_xZn_{1-x}Fe_2O_4$, x =0.5, 1 is shown in fig (4)

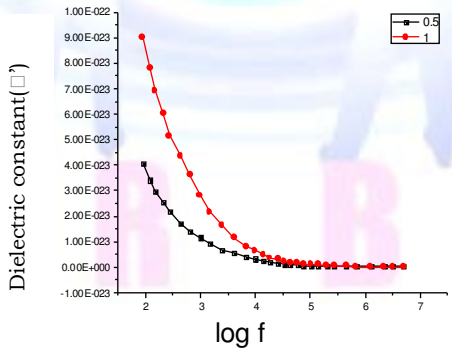

Fig4. Effect of frequency on dielectric constant (□') at room temperature $Mn_xZn_{1-x}Fe_2O_4$, x = 0.5, 1.

The dielectric constant is found to be less than bulk sample for a frequency of 100 KHz at room temperature. The decrease in dielectric constant with increase in frequency is attributed to the fact that the electron exchange between fe^{3+} and fe^{2+} ions cannot follow the change of the external applied field beyond certain frequency [11]. This low dielectric loss is attributed to homogeneity better symmetry and small grain size when compared with bulk sample [12]. Small grain have large surface boundaries and are the regions of high resistance this reduces the interfacial polarization. From the figure it is clear that the dielectric constant decreases with

increase in frequency.showing dispersion in low frequency range. All samples show dispersion due to Maxwell-Wangner [13- 14] and are also in agreement with the Koop's phenomenological theory [6]. The decrease in dielectric constant at higher frequency can be explained on the basis that the solid is assumed as composed of well conducting grains and is separated by nonconducting grains boundaries.When electron reach such non conducting grain boundaries through hopping the resistance of the grain boundry is high. Hence the electron pile up at the grain boundaries and produce polarization. At higher frequency beyond a particular limit, the electron does not follow the alternating field.this decreases the probability of electrons reaching the grain boundary and as a result polarization decreases [13,6].This decreases the hopping and hence decreases the polarization up to X=0.5.increase in dielectric constant for the concentration X=1 may be due to the formation of Fe^{3+} ions in octahedral site.the increase in Fe^{3+} ion in octahedral site increases the hopping between Fe3+ and Fe2+ and hence polarization increases this result attributed in the local displacement of electrons in the direction of applied field thereby increasing the dielectric constant.

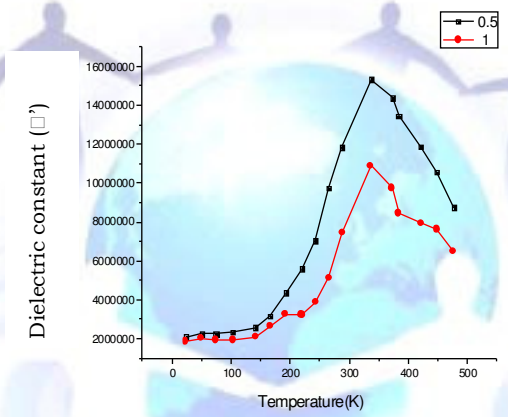

Fig.5. Variation of dielectric constant (□') with temperature at 1MHz for $Mn_xZn_{1-x}Fe_2O_4$, x =0.5, 1.

Figure 5. Shows the variation if dielectric constant 1MHz with temperature for mixed $Mn_xZn_{1-x}Fe_2O_4$, x =0, 0.5, 1. The dielectric constants were found to decreases continuously. This temperature called as transition temperature (Td).this type of similar temperature variation of the dielectric constant has been reported by M.A. Ahmad [15] this change in the dielectric behaviour beyond transition temperature may be due to polarizability increasing and the thermal energy is quite sufficient to liberate some charge carriers the field accompanied with applied frequency (1MHz) aline them in its direction leading to an increase in dielectric as a result of co-operation between orientational and rotational polarization. The electron hopping between Fe3+ and Fe2+ is expected to be increased, helping in increasing dielectric constant until reaching the curie temperature. above 350K the thermal energy due to heating is high enough to overcome the field effect as well as disturbing the ordered dipole thus decreasing dielectric constant [15].

5.2. Dielectric loss:

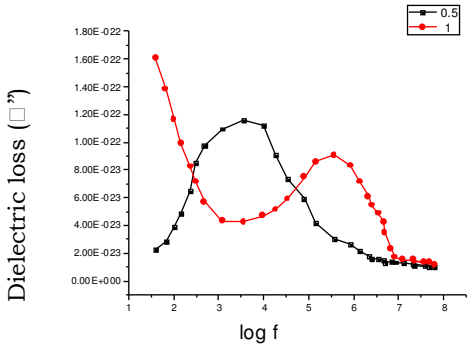

Fig 6. plot of dielectric loss tangent with frequency for $Mn_xZn_{1-x}Fe_2O_4$, x =0.5, 1.

Fig.6. shows the variation of dielectric loss tangent tan(δ) with frequency at room temperature in all the cases there is decrease in dielectric loss initially followed by resonance peak with increase in frequency.the occurrence of peak in the variation of loss tangent with frequency can observed when the hopping frequency of localized charge carrier is approximately equal to that of the externally applied electric field i.e. resonance phenomena.From the fig. it can be seen that the composition between X=0 and X=1.tan(δ) shows a maximum resonance peak at frequency between 10 and 50 KHz. Iwauchi [7] reported a strong correlation between the conduction mechanism and the dielectric behaviour of the ferrites.The conduction mechanism is considered as due to hopping of electrons between Fe3+ and Fe2+ resulting in local displacement which determines the polarization behaviour of the ferrite [16].the conduction for observing a maximum in tan(δ)of a dielectric material is given by [17].

$$\omega\tau \; \square \; 1 \qquad \text{----------} \qquad (1)$$

Where τ is the relaxation time And $\omega = 2\pi f_{max}$

Where f_{max} is proportional to the hopping probability 'P'. The relaxation time 'τ' is related to the hopping probability per unit time P by an equation $\tau = \frac{1}{2}P$ or $f_{max} \alpha P$

Now decrease of f_{max} with increase magnese concentration indicates that the hopping probability per unit time decreases [paper].

5.3. A C Conductivity

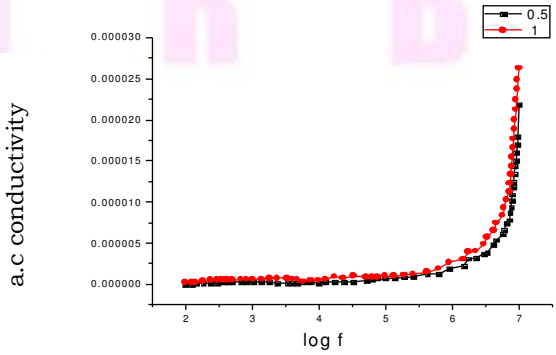

Fig.7. shows the ac conductivity with frequency at 300K. $Mn_xZn_{1-x}Fe_2O_4$, x =0.5, 1.

In fig.7 Shows the entire sample shows increase in conductivity with increase in frequency which is the normal behaviour of the ferrites.The dispersion in conductivity with frequency has been explained by Koop's theorm [6] which suggested that the ferrite compact act as a multilayer capacitor.the effect of the multilayer condenser

rise with frequency as a result the conductivity increases or in other word the conduction mechanism in ferrite can be explained on the basis of hopping of charge carriers between Fe^{3+} □ Fe^{2+} ions on octahedral sites.

6. Conclusions

$Mn_xZn_{1-x}Fe_2O_4$, x=0,0.5,1. have been synthesized using the sol-gel autocombustion method. The formation of the ferrite powder has been confirmed by XRD studies. And the particles size is found to be15nm & 16nm by using the Debye Scherrer formula which is close agreement with the TEM result 28 nm. The general trand of □' and □" for all composition of the sample decreases with increasing frequency.and the value of the dielectric of the sample is found to be less which is most useful for the higher frequency application. The charge libration and electron hopping together form the basis for the conduction mechanism in $Mn_xZn_{1-x}Fe_2O_4$, x=0, 0.5, 1.ferrites.

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