Dielectric Properties of Mixed Ferrite ($Mn_{0.4}Zn_{0.6}Fe_2O_4$ and $Co_{0.4}Zn_{0.6}Fe_2O_4$) Composites

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Abstract

Soft ferrite ($Mn_{0.4}Zn_{0.6}Fe_2O_4$) and hard ferrite ($Co_{0.4}Zn_{0.6}Fe_2O_4$) nanocomposites (x $Mn_{0.4}Zn_{0.6}Fe_2O_4$ + (1-x) $Co_{0.4}Zn_{0.6}Fe_2O_4$ (where x= 0.25, 0.5, 0.75) were prepared with different weight percent. Crystal structures and microstructures of these composites have been investigated by using X-ray diffraction and scanning electron microscope for composite samples sintered at 900°C/30 min using microwave sintering technique. The effect of composite weight percent on dielectric properties of composites are examined over a wide frequency range (1MHz-1.8GHz) by studying the real and imaginary part of permittivity with available theories. Investigation show variation of mixed ferrites for resistivity and resonating frequency.

Keywords: Ferrites, Microwave sintering, Dielectric properties.

INTRODUCTION

Ferrimagnetic materials allows the fine tuning of the absorbing characteristics which are often limited by operating frequency, curie temperature, anisotropy of materials, operating parameters of ferrites as reported by several researchers [1-3]. Auzans et al. [4] have studied properties of Mn–Zn ferrite nanoparticles used for ionic and surfaced ferrofluids with different degrees of zinc substitution prepared by co-precipitation method. Chandana Rath et al. [5] have reported the dependence of cation distribution of particle size, lattice parameter and magnetic properties in nanosize Mn–Zn ferrite for different degrees of Zn substitution prepared by hydrothermal precipitation method. The ferrites such as Mn-Zn ferrites and Co-Zn ferrites contain a high quantity of nonmagnetic zinc ions which lowers the Curie temperature and moderates the thermo stability used for various applications such as transformers, spintronics etc [6-8]. Knowledge of electrical properties such as resistivity, dielectric constant and dielectric loss is important for processing of elements useful for electronic circuits since ferrites play useful role in many areas [6].

The microwave hydrothermal synthesis yields low particle size with higher densification [9]. Microwave sintering technique prevents low loss during sintering processing with improvement of properties [10]. Hence, for present work, nanopowders of $Mn_{0.4}Zn_{0.4}Fe_2O_4$ [11] and $Co_{0.4}Zn_{0.6}Fe_2O_4$ [12] are synthesized using microwave hydrothermal system. Mn-Zn ferrites is considered of magnetic nature with high permeability with low losses [13,15]. Zinc in cobalt ferrite promises to be important class for studies in elastic properties useful for transducers applications [14]. D.c. resistivity is measured under room temperature conditions using Kethley ammeter. The dielectric properties such as real part of permittivity ($ε'$) and imaginary part of permittivity ($ε''$) are measured for wide frequency range on the sintered composite samples and obtained results have been discussed. The present work is an attempt to understand the effect of mixing the ferrite-ferrite composite on real part of permittivity and imaginary part of permittivity up to frequency range of 1.8 GHz.

EXPERIMENTAL WORK

The nanopowders of $Mn_{0.4}Zn_{0.4}Fe_2O_4$ [10] and $Co_{0.4}Zn_{0.6}Fe_2O_4$ [11] are synthesized using microwave hydrothermal system as reported elsewhere. The synthesized nano powders of $Mn_{0.4}Zn_{0.6}Fe_2O_4$ and $Co_{0.4}Zn_{0.6}Fe_2O_4$ are mixed at different weight percentage (%) to prepare the composites of x $Mn_{0.4}Zn_{0.6}Fe_2O_4$ + (1-x) $Co_{0.4}Zn_{0.6}Fe_2O_4$ where 0.25, 0.5, 0.75 and then and named as sample A (x=0.75), sample B (x=0.50) and sample C (x=0.25) . The samples are thoroughly mixed with agate mortar and then mixed with 2wt% polyvinyl alcohol as a binder. Then the powders are uniaxially pressed at a pressure of 1500 kg/cm^2 to form pellet (~1 mm in thickness, ~10 mm diameter) specimens. The samples are sintered by using microwave furnace at 900ºC for 30 minutes. The d.c. resistivity (ρ) of the present samples, at room temperature is measured using a two probe method. The complex permittivity (ε*) of the composite samples was measured over a wide frequency range of 1MHz to 1.8 GHz using Agilent 4291B Impedance analyzer.
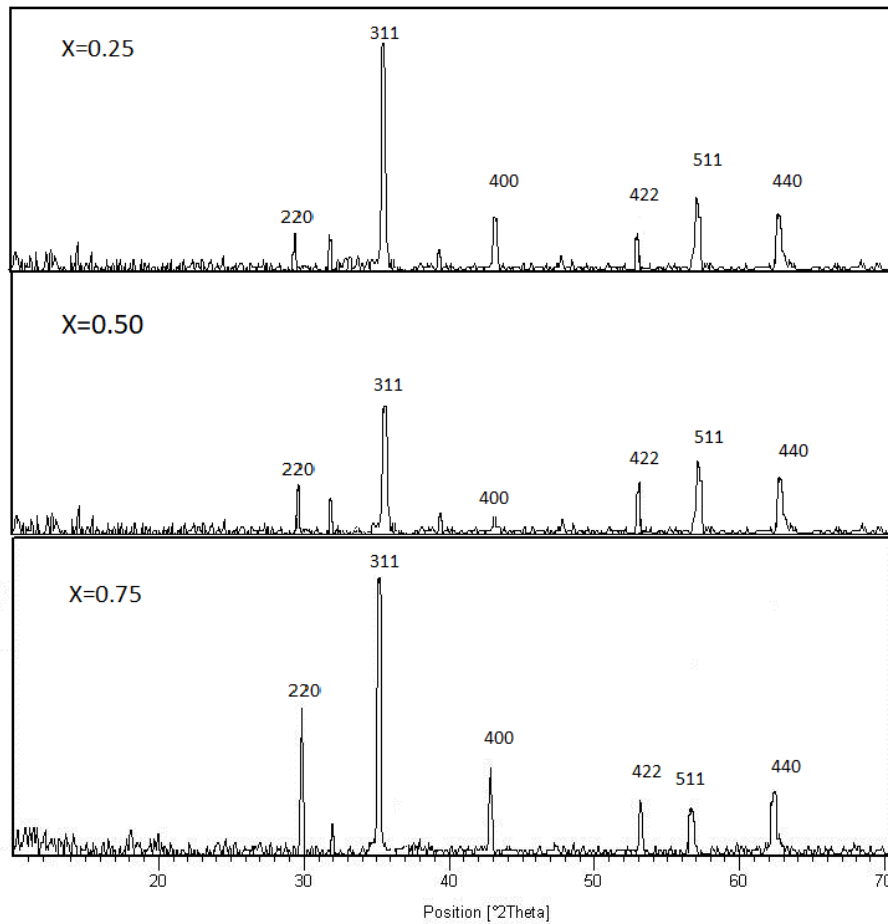
Figure 1. X ray diffraction pattern for composite ferrite samples.

In the present investigation, phase identification of the sintered samples are performed by the powder X-ray diffraction with a Philips (Panalytical) X-ray diffractometer with Cu K_α radiation ($\lambda = 1.5406$ Å). The ferrites are compared with the standard ICDD data for $Mn_{0.4} Zn_{0.6} Fe_2O_4$ (74-2400) and CAS number for cobalt ferrite (22-1086) and zinc ferrite (89-1012). The XRD pattern suggests that the samples are having spinel phase of ferrite without any impurities or secondary phases even after mixing the two different ferrites compositions and sintering at high temperatures. The lattice parameter for the microwave sintered samples is calculated and tabulated in table 1. The results suggests that the lattice parameter increases (8.347 A° to 8.388 A°) with increase in the manganese content in the composite ferrite. Manganese has higher atomic radius when compared with cobalt or iron which are located in the octahedral sites and zinc radius which is present in the tetrahedral sites. It can be observed from the Table 1 that a low porosity value of 5% is obtained for the sample microwave sintered samples at 900°C/30 min. The grain size is estimated around 75 nm to 97 nm estimated from SEM (Fig.2) as shown in Table1. The increase in grain size may be due to increase of manganese ions which is having higher ionic radius.
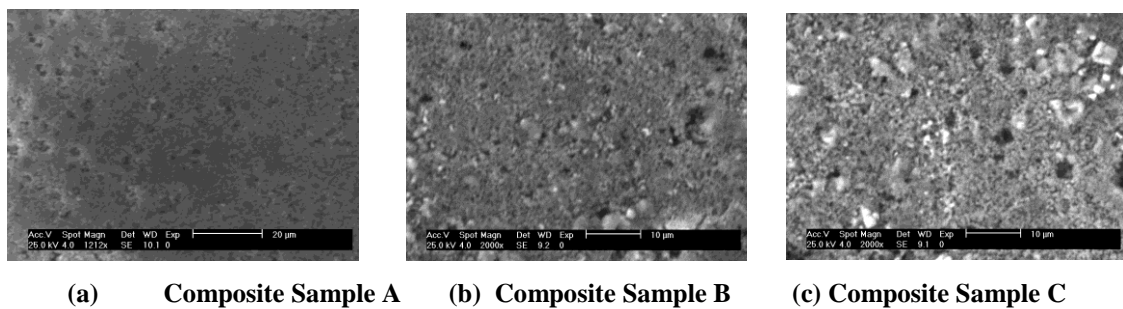
| (a) | **Composite Sample A** | (b) | **Composite Sample B** | (c) | **Composite Sample C** |

Figure 2. Sintered SEM Pictures for the composite samples

D.c resistivity values of the microwave sintered sample are presented in the table 1. It can be observed that the Sample A has highest resistivity than the other two samples. This may be due to presence of less manganese ions and more number of cobalt ions. The low resistivity in the sample B and sample C is due to reduction of Mn^{2+} content.   The Fe^{2+}, Co^{2+} ions show strong preference to octahedral sites i.e., B-sites. Since Co^{2+} ions present with Fe^{3+}, it is possible that some of these ions can be oxidized to Co^{3+} ions during the sintering [6,16]. The conduction mechanism in ferrites can be understood on the basis of hopping of electrons and understood using Verwey theory [17-18].   Microwave sintering due to rapid processing technique gives little time for material loss. D.c. resistivity depends on the micro structural depends on the properties such as grain size, porosity etc. Smaller grains shows greater surface to volume ratio by which higher oxidation and reconversion of ions takes place. The smaller grains effect in greater number of grain boundaries, which further acts as acts as scattering center for the flow of electrons leading to rise of resistivity [10, 19]. Many researchers have found the behavior of resistivity dependent on sintering conditions, temperature along with density of the samples [20-21].

Table 1: Room temperature values for the composite ferrites.

Sample	D.C. Resistivity ($\rho_{d.c}$) $\times 10^8\ \Omega.m$	X ray density (ρ_{xray}) gm/cm^3	Bulk Density ρ_{Bulk} gm/cm^3	Lattice parameter(a) A^o	Porosity (%)	Grain size from SEM (nm)
A	10.68	5.437	5.157	8.347	5.15	75
B	9.75	5.384	5.062	8.370	5.86	90
C	8.48	4.975	4.714	8.588	5.32	97

The frequency dependence of real part of permittivity (ε') and imaginary part of permittivity (ε″) for microwave sintered composite ferrites is shown in Fig.3 and Fig.4. It can be seen the variation of dielectric constant decreases with increasing in frequency. It can be seen from Table 1 that the value of ε' for microwave sintered composite ferrites is 7 (sample A) at 1 MHz and remains constant up to 900 MHz. With further increase of frequency, the value of ε' also found to increase and shows a dispersion peak above 1.5 GHz. The lower value of dielectric constant [22] in sample A is due to reduction of interfacial polarization which occurs in smaller grains which acts high resistances grain boundaries regions. With increase in manganese content, resistance decreases which results in increases dielectric constant. With increase in grain size, due to interfacial polarization there is rise in dielectric constant as shown in table 1.
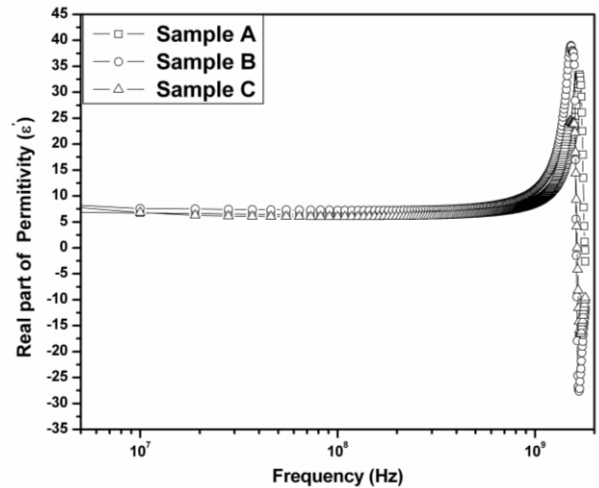

Figure 3. Dependence of dielectric constant (ε′) on frequency for Composite ferrites

Variation of dielectric in ferrites is often understood on the basis of Maxwell theory, which uses two layer structure [23]. These layer are often separated by series of conducting and non conduting layer with high surface area. When the electrons reach grain boundaries by hopping mechanism from one site to another; they pile up and produce polarization. With increase of applied frequency, the probability of hopping of electrons between the grains and polarization decreases. Iron ion (Fe^{2+}/Fe^{3+}) in octahedral sites does not follow the electric field for which dielectric constant is low even with the increase in frequency [24]. But above 1 GHz, dielectric constant increase and thus resonance is observed. Resonance at high frequency indicates the important role of ionic polarization or electronic polarization with ferrite grains [25] . Increase in cobalt content is compensated by substitution of manganese ions which decreases migration of ions (Fe^{2+} and Fe^{3+}) from octahedral sites or tetrahedral sites (Mn^{2+}/Mn^{3+} or Co^{2+}/Co^3). The decrease in the hopping mechanism [26] increases the resistance which is due to charge accumulation thus manifesting in lower permittivity values.
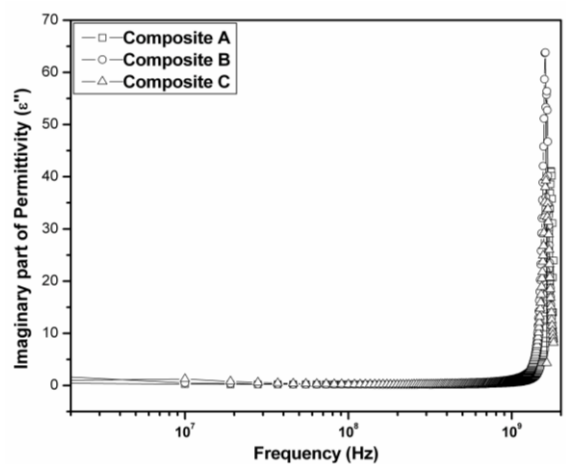

Figure 4. Dependence of dielectric loss (ε″) on frequency for Composite ferrites .

The absorption characteristics of ferrites are given as measurement of dielectric loss (ε'') as shown in the Fig. 4. The dielectric loss behavior for the observed samples is low and losses observed above 1.5 GHz is due to resonance. Intensity of the peak decreases with hard ferrite and shift is observed towards lower frequency. Dielectric loss gives an indication of loss energy in the sample which may be due to domain wall contribution at lower frequency and spin resonance in higher frequency. The relaxation occurs when hopping frequency of electron matches with applied frequency, it results in resonance and increase in losses. Dielectric loss occurs due to polarization when it lags behind the applied field and losses are contributed by the electron hopping or defect dipoles. The hopping mechanism contributes losses at lower frequency therefore it can be said that the defect dipoles plays a part at higher frequency for which values are very low. The appearance of resonance peak towards lower side of frequency band indicates the hindrance that causing to rotation of dipole due to strengthening of dipole-dipole interaction. A survey of literature tells that many papers have been published on the dielectric dependence on frequency in the case of ferrites [27-29].

CONCLUSIONS

Mixed composite of $Mn_{0.4}Zn_{0.6}Fe_2O_4$ and $Co_{0.4}Zn_{0.6}Fe_2O_4$ ferrite are prepared by adding different weight percentages and submitted for microwave sintering method. It is found that the value of real part of permittivity (ε') and imaginary part of permittivity (ε'') remained low and constant for wide frequency range with good resistivity in the samples. The results indicate that ferrite-ferrite composite may be used for frequency operated devices.

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