



Preparation and study of dielectric properties of $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$ Nano particles

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ABSTRACT

$\text{Co}_{0.5}\text{Mn}_{0.25}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$ nanoparticles of average size of 61 nm were prepared by chemical co-precipitation method which could be used for ferrofluid preparation. The composition is characterized by X-ray diffraction technique (XRD). XRD study shows formation of single phase homogeneous compound with cubic structure. The crystal size was calculated from XRD data by using Scherrer equation and is confirmed by SEM, which reveals the formation of nanocrystalline ferrite. The dielectric constant and dielectric loss dependence on doping level and frequency at room temperature were described in detail. The leakage current properties of $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$ nanoparticles were also discussed.

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Introduction

Ferrimagnetic cubic spinels namely ferrites possess properties of both magnetic materials and electric insulator. These properties make ferrites as an important material in many technological applications. From application point of view, ferrites have shown multi-functional character and properties that can be tailored for making micro-electric devices, magnetic sensors, magnetic switches, electro-magnetic circuits and microwave devices (Jun Y.-wook *et al.*, 2007).

Among spinel ferrites, cobalt ferrite, CoFe_2O_4 is especially interesting because of its high cubic magnetocrystalline anisotropy, high coercivity and moderate saturation magnetization. Recently, cobalt ferrite nano particles were also known to be a photo-magnetic material, which shows interesting light-induced coercivity change [1, 2]. Also Co-Zn ferrite found to possess good elastic properties [3]. In this present study, the preparation of $\text{Me}_{1-x}\text{Mn}_y\text{Zn}_y\text{Fe}_2\text{O}_4$ fine particles, where $\text{Me} = \text{Co}^{2+}$ with ($x=0.5$, and $y=0.25$) with average crystallite size 64nm by chemical co-precipitation method and the consequent change in their lattice parameter, particle size, dielectric behavior at room temperature were reported. Low leakage current density of cobalt doped ferrites will enhance the good polarization hysteresis (P-E) loop and a large remnant polarization which in turn improves the ferroelectric properties[11].

Synthesis and characterization $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$ of nanoparticles

Ultra fine particles of $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$ were prepared by co-precipitating aqueous solutions of CoCl_2 , MnCl_2 , ZnCl_2 and FeCl_3 mixtures respectively in alkaline medium. The mixed solution of CoCl_2 , MnCl_2 , ZnCl_2 and FeCl_3 in their respective stoichiometry (100 ml. of 0.5 M CoCl_2 , 100 ml. of 0.25 M

ZnCl_2 , 100 ml. of 0.25 M MnCl_2 and 100 ml. of 2 M FeCl_3 in the case of $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$ and similarly for the other values of x) was prepared and kept at 333K (60°C). This mixture was added to the boiling solution of NaOH (0.63 M dissolved in 1200 ml. of distilled water) within 10 seconds under constant stirring. Nano ferrites are formed by conversion of metal salts into hydroxides, which take place immediately, followed by transformation of hydroxides into ferrites. The solutions were maintained at 358K (85°C) for one hour. This duration was sufficient for the transformation of hydroxides into spinel ferrite (dehydration and atomic rearrangement involved in the conversion of intermediate hydroxide phase into ferrite) [4]. Sufficient amount of fine particles were collected at this stage by using magnetic separation. These particles were washed several times with distilled water followed by acetone and dried at room temperature. The powder sample was palletized at the pressure of 300kg/cm^2 to yield a pellet of 10mm diameter and 2mm thickness.

XRD and SEM:

The X-ray diffraction (XRD) patterns of the samples were recorded on a BRUKER-binary V2 (RAW) powder diffractometer using $\text{Cu K}\alpha$ ($\lambda=1.54060 \text{ \AA}$) radiation. Slow scans of the selected diffraction peaks were carried out in step mode (step size 0.02° , measurement time 5s, measurement temperature 323K (25°C), standard: Si powder). The particle size of the ferrite sample was obtained from broadening of XRD peak by using the Scherrer equation [5], and it was found to be 64nm Fig.(1).

$$D_{\text{XRD}} = \frac{0.89\lambda}{\beta \cos\theta}$$

where λ - wavelength of X-ray used in $\text{\AA}$, β - FWHM in radians in the 2θ scale, θ - the Bragg angle, D_{XRD} - crystallite size in nm. Co substituted Mn-Zn ferrite has a spinel structure. It is evident from the particle size that wet chemical co-precipitation method yields the particles of the order of nanometer dimension. The particle size was confirmed by SEM data (Fig. 2).

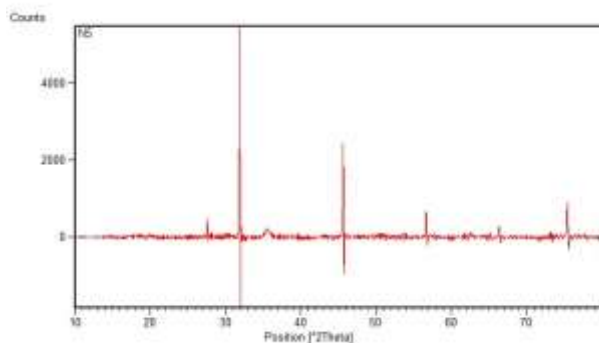


Fig. 1. X-ray diffraction pattern for $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$

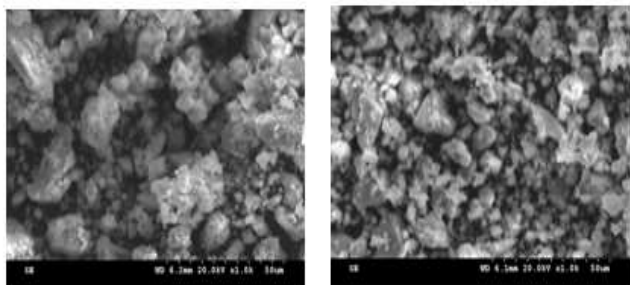


Fig.2. SEM images of $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$

Dielectric properties:

The dielectric properties of $\text{Co}_{1-x}\text{Mn}_y\text{Zn}_y\text{Fe}_2\text{O}_4$ with $x = 0.5$ and $y=0.25$ were studied using HIOKI 3532-50 LCR HiTESTER. Dielectric loss, dielectric constant were computed according to Smit and Wijn [6] as a function of frequency.

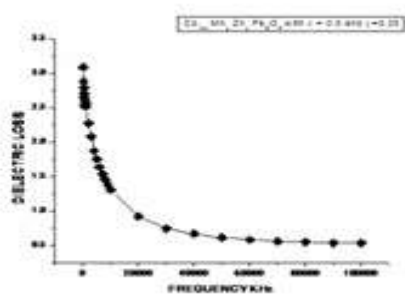


Fig.3 Variation of dielectric loss with frequency

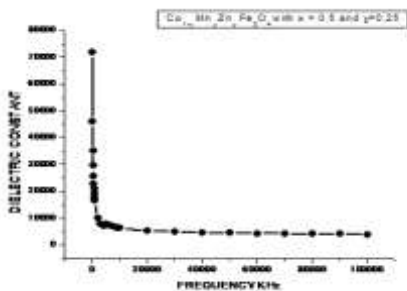


Fig 4. Variation of dielectric constant with frequency

Fig. 3 and Fig.4 show that dielectric constant as well as dielectric loss decreases with increasing frequency exhibiting normal ferrimagnetic behavior. A more dielectric dispersion is observed at lower frequency region and it remains almost independent of applied external field at high frequency. Similar behavior of dielectric constant with frequency was observed by many researchers [7, 8]. The dielectric dispersion observed at lower frequency region is due to Maxwell- Wagner [9] interfacial type of polarization, which is in agreement with Koops phenomenological theory [10]. The decrease in dielectric constant with frequency can be explained by the supposition that the mechanism of polarization process in ferrite is similar to that of conductivity process. By the electronic exchange, $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$, one can obtain local displacement of electrons in the direction of electric field. These displacements determine the polarization in ferrites. It is known that effect of polarization is to reduce the field inside the media. The decrease of polarization with increase in frequency may be due to the fact that, beyond a certain frequency of the electric field, the electronic exchange between ferrous and ferric ions cannot follow the alternating field. Hence dielectric constant may decrease substantially as frequency is increased. The variation of dielectric constant with concentration at a frequency of 10KHz was studied. Fig.5.shows that as cobalt was increased the dielectric constant was found to be decreasing.

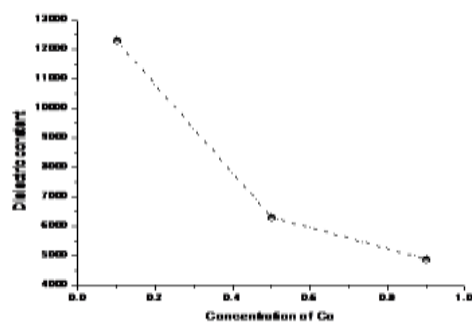


Fig.5. Variation of dielectric constant with concentration at a frequency of 10KHz

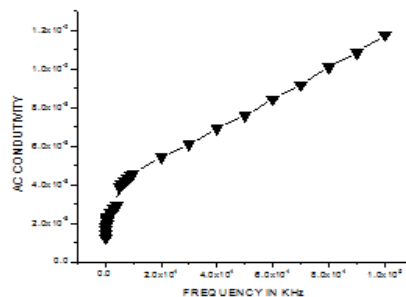


Fig.6. Variation of AC conductivity with frequency

Fig. 6 shows the variation of σ_{ac} with frequency. It is noted that σ_{ac} increases with increase in frequency. At lower frequency, the grain boundaries are more active, hence the hopping frequency of electrons between Fe^{3+} and Fe^{2+} ions is less. At higher frequencies, the conductive grains become more active by promoting the hopping of electrons between Fe^{3+} and Fe^{2+} ions therefore increasing the hopping frequency [11]. So we observe the increase in conductivity with the increase in frequency. The linearity of the plots is attributed to small polaron type conduction [12].

Leakage current properties

The V-I characteristics of $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$ was studied using KEITHLEY 6517A Electrometer/High Resistance Meter. The characteristics of the leakage current density versus applied electric field (J/E) for the $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$ are shown in Fig. 7. The J/E curve has good symmetry under positive and negative electric fields. At an applied electric field of 0.023742 KV/Cm, the leakage current density of $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$ is about $9.30 \times 10^{-6} \text{ A/cm}^2$, which is very low.

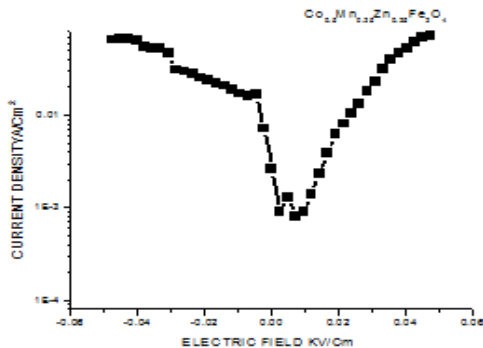


Fig.7. Variation of current density with Electric field

Results and conclusions:

The particles size synthesized by co-precipitation method was found to be in nanosize. The dielectric loss and dielectric constant are frequency dependent. As frequency increases both dielectric constant and dielectric loss decreases. Dielectric constant decreases as the cobalt content increases. It is noted that

ac conductivity σ_{ac} increases with increase in frequency. The leakage current density of $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Zn}_{0.25}\text{Fe}_2\text{O}_4$ is about $9.30 \times 10^{-6} \text{ A/cm}^2$, at an applied field of 0.023742 KV/Cm which is very low.

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