

Electric and Dielectric Study of Zinc Substituted Cobalt Nanoferrites Prepared by Solution Combustion Method

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Abstract In the present work, zinc substituted cobalt nanoferrites, with formula $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$), have been prepared by solution combustion method and are investigated for their electric and dielectric properties such as dc resistivity, dielectric constant and dielectric loss. Analysis of the X-ray diffraction pattern of all the samples confirmed the formation of spinel structure. The surface morphology of the samples is studied by using TEM. The dc resistivity was found to be increasing with an increasing substitution of zinc ions and the high value of dc resistivity, $10^8 \Omega \text{ cm}$, make these nanoferrites more suitable at high frequency applications. Dielectric constant and dielectric loss tangent, measured in the frequency range from 1kHz to 1MHz, are found to be decreasing with an increase in frequency. Possible mechanisms responsible for the results are discussed minutely in this paper.

Keywords: DC resistivity, dielectric properties, nanoferrites

1. Introduction

Spinel ferrites have been studied extensively because they play a vital role in the technological applications. Ferrites have good electric properties and a large number of applications from microwave to radio frequency [1]. The dielectric properties of these ferrites are very sensitive to the method of preparation and sintering condition. Therefore, the selection of an appropriate process is the key to obtain high quality ferrites [2]. The ability to prepare nanostructures with defined morphologies and sizes in large scale is an essential requirement for applications in nanomaterials. As a result, extensive efforts have been devoted to develop synthetic capabilities to produce nanomaterials with tailored magnetic and electrical properties [3]. The properties of nanomaterials are remarkably different from that of their bulk counterpart. The interest in ferrite nanoparticles is due to their important physical and chemical properties and potential for various technological applications such as high density magnetic storage, electronic and microwave devices, sensors, magnetically guided drug delivery etc [4]. Cobalt ferrite is a hard magnetic material having cubic spinel structure and attracted considerable attention of the scientific community due to which it can be used as one of the competitive candidates for specific applications such as high density audio and video recording media, for controlled drug delivery, radio frequency hyperthermia, magnetic resonance imaging (MRI) and medical diagnostics [5]. Among various ferrites, ZnFe_2O_4 and CoFe_2O_4 have been most extensively studied systems, because they exhibit the typically normal and inverse spinel ferrites respectively. Zinc ferrite bulk is anti-

ferromagnetic below the Neel temperature ($T_N = 10\text{K}$) and turns to ferromagnetic or super paramagnetic when particle size reduces to a nanoscale [6]. In ZnFe_2O_4 , zinc ions occupy the tetrahedral sites and all Fe^{3+} ions occupy the octahedral sites. In contrast, CoFe_2O_4 exhibits ferromagnetism where cobalt ions occupy the octahedral sites and Fe^{3+} ions are equally distributed in tetrahedral and octahedral sites. Therefore, Co-Zn mixed ferrite has attracted considerable attention due to the completely different and interesting properties of ZnFe_2O_4 and CoFe_2O_4 . A large number of methods has been developed to prepare $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ (CZFO) ferrite nanoparticles, such as the Co-Precipitation [7], Ceramic technique [8], Microwave Combustion method [9], Sol-gel method [10], Solvothermal method [11], the standard solid-state reaction technique [12] and the PEG-assisted hydrothermal method [13]. Further, the electrical and dielectric properties of cobalt-zinc nanoferrites were reported by many workers [14,15,16,17]. Although there are reports on the electric and dielectric behavior of Co-Zn ferrites but, rarely any work has been reported on electric and dielectric properties of $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ prepared by solution combustion method. Thus, in this paper for the first time we are reporting the electrical and dielectric properties of Co-Zn ferrite nanoparticles synthesized by solution combustion method.

2. Experimental Details

$\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrite nanoparticles where $x = 0.0, 0.1, 0.2$ and 0.3 , are synthesized via solution combustion technique. The chemical reagents used in this work are Ferric nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Zinc nitrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and Urea

$\text{CO}(\text{NH}_2)_2$ as a fuel. All reagents are of analytical grade. In a stoichiometric ratio $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Urea are mixed in distilled water to obtain precursor solutions. The obtained precursor solution then heated on a hot plate up to drying of the solution with evolution of large amount of gases (N_2O and CO_2) and then the solution starts to burn with release of lots of heat. The whole procedure takes place for minimum 2-3h. The obtained powder samples are annealed at 500°C for 4h. X-Ray powder diffraction analysis is conducted on XPERT-PRO Diffractometer (XRD) using Cu K_α radiations. The dc electrical resistivity is obtained by a simple two probe method using Keithley Electrometer (Model 2611A). The dielectric measurements of the samples are carried out in the frequency range from 1kHz to 1MHz by using Impedance Analyzer (WAYNE KERR 6500B).

3. Results Analysis

3.1. Structural Analysis

Figure 1 shows the XRD patterns for all the samples of $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$, $x=0.0, 0.1, 0.2$ and 0.3 , nanoferrites. The figure shows a typical cubic spinel structure. The diffraction peaks are broad because of the nanometer size of the crystallite.

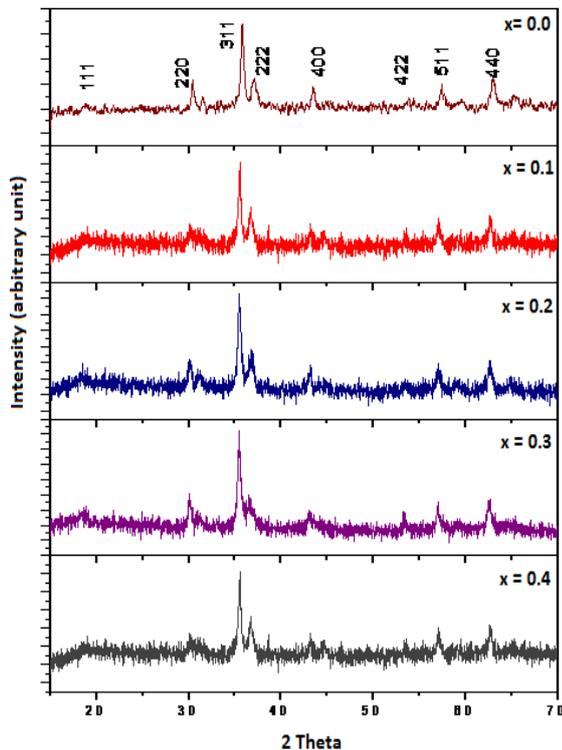


Figure 1. XRD patterns of $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoferrites

The crystallite size of the samples is estimated from the broadening of the XRD peaks using the Scherrer formula [18].

$$D = 0.9\lambda / \beta \cos\theta \quad (1)$$

where D is crystallite size, β is full width at half maximum (FWHM) of the (311) peak, λ is X-ray wavelength and θ

is diffraction angle. The lattice parameter (a) was calculated by using the following relation:

$$a = (\lambda/2\sin\theta) (h^2+k^2+l^2)^{1/2} \quad (2)$$

Average crystallite size for all samples was obtained as 29nm, 25nm, 24nm, 22nm and 21nm for $x = 0.0, x = 0.1, x = 0.2, x = 0.3,$ and $x = 0.4$ respectively. The crystallite size was found to be decreasing with the increasing substitution of zinc ions. This is due to the fact that the radius of Co ions is smaller than that of Zn ions. Therefore as the concentration of Zn ions increases the lattice constant also increases. Further, an increase in the lattice constant was noticed with the increasing substitution of zinc ions.

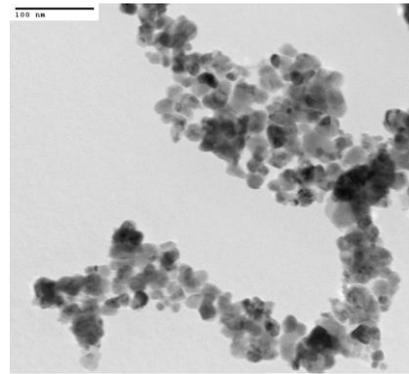


Figure 2. TEM image of $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ nanoferrite

Figure 2 shows TEM micrograph for $x=0.4$ sample. It can be seen that the particles are quite well dispersed and not much agglomerations are present. The detailed structural analysis is presented by the author elsewhere [19].

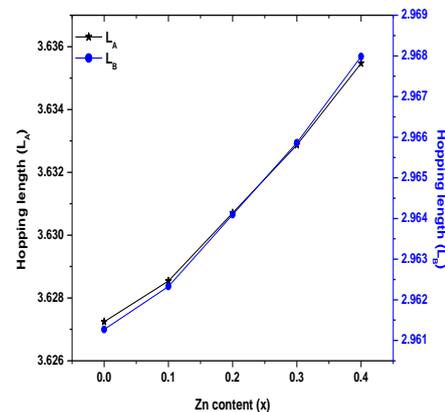


Figure 3. Variation of hopping length (L_A and L_B) with composition x for $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$

The distance between magnetic ions at tetrahedral A (L_A) and octahedral B (L_B) sites was calculated by using the following relations [12].

$$L_A = 0.433a \quad (3)$$

$$L_B = 0.354a \quad (4)$$

The variation of hopping length L_A and L_B is also shown in Figure 3. Both L_A and L_B increases with an increasing substitution of Zn^{2+} ions. This may be attributed to the increase in lattice constant of the samples.

3.2. DC Resistivity

Figure 4 shows the variations of dc resistivity with zinc concentration. It is evident from the figure that dc resistivity is increasing with the increasing content of zinc ions. The observed variations in resistivity can be explained by Verwey's hopping mechanism [20]. According to Verwey, the electronic conduction in ferrites is primarily because of hopping of electrons between ions of same element present in more than one valence state, distributed randomly over crystallographically equivalent lattice sites [21]. Ferrites structurally form cubic close packed oxygen lattices with the cations at the octahedral (B) and the tetrahedral (A) sites. The distance between two metal ions at octahedral sites is smaller than the distance between a metal ion at an octahedral site and another metal ion at a tetrahedral site. The electron hopping between octahedral and tetrahedral sites under normal conditions therefore has a very small probability compared with that for B–B hopping. Hopping between tetrahedral and tetrahedral sites does not exist for the simple reason that there are only Fe^{3+} ions at the tetrahedral sites and any Fe^{2+} ions formed during processing preferentially occupy octahedral sites only. Further, the hopping probability depends upon (a) the separation between the ions involved and (b) the activation energy. As Zn^{2+} ions strongly prefers to occupy A-sites [22], while cobalt ions partially occupy A-sites and B-sites. Thus, when Zn^{2+} ions increases at A-sites then some of the Fe-ions from B-sites will migrate towards the A-sites as a result the number of Fe^{2+} and Fe^{3+} ions at B-sites, which are responsible for electrical conduction in ferrites, will decrease.

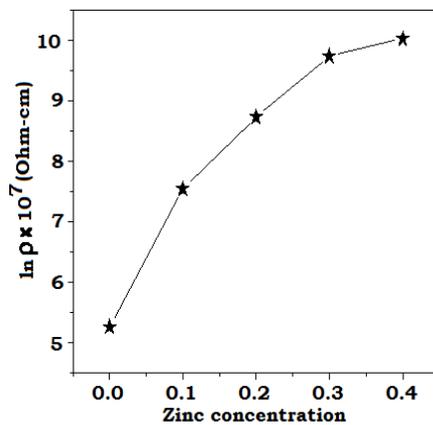


Figure 4. Variations of dc resistivity of $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoferrites with zinc content

This will limit the degree of conduction by blocking the Verwey's hopping mechanism resulting thereby an increase in resistivity. Further, the room temperature dc resistivity is of the order of $10^8 \Omega$ which makes these nanoferrites suitable for microwave applications.

3.3. Dielectric Constant

The value of dielectric constant is calculated by using the following relation:

$$\epsilon = C_p d / \epsilon_0 A \quad (5)$$

where ϵ_0 is the permittivity of free space, d is the thickness of the pellets, A is the area of cross-section of the pellet

and C_p is the measured value of the capacitance of the pellet. Figure 5 shows the variation of dielectric constant as a function of frequency at room temperature from 1 kHz to 1 MHz. It is observed that for each sample the dielectric constant decreases with an increase of frequency and becomes constant at higher frequency. The decrease of the dielectric constant with an increase of frequency as observed is a normal dielectric behavior of spinel ferrites and can be explained by the phenomenon of dipole relaxation. Dipole relaxation refers to the relaxation response of a dielectric medium to an external electric field. Relaxation, in general, is a lag in the response of a system. It is well known that in ferrites with heterogeneous structure the samples consist of well-conducting grains separated by poorly conducting grain boundaries [23]. The electrons reach the grain boundary through hopping and if the resistance of the grain boundary is high enough, electrons pile up at the grain boundaries and produce polarization. However, as the frequency of the applied field is increased, the electrons reverse their direction of motion more often. This decreases the probability of electrons reaching the grain boundary and as a result polarization decreases. Therefore, the dielectric constant decreases with increasing frequency of the applied field [24].

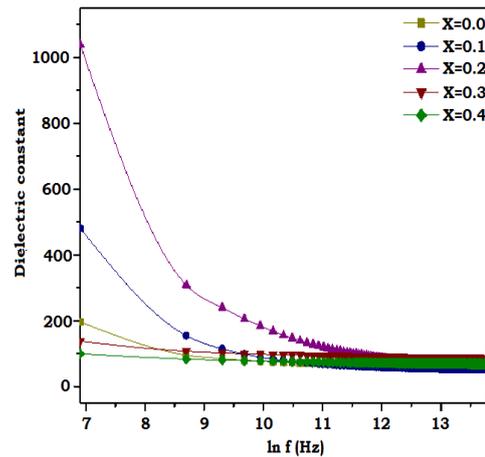


Figure 5. Variations of dielectric constant with frequency of $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoferrites

Also, from the Figure 5 it is quite clear that dielectric constant decreases beyond $x=0.2$. This can be explained on the basis of mechanism of polarization process which is similar to that of conduction process. The whole polarization in ferrites is mainly contributed by space charge polarization, the conductivity in materials and hopping exchange of the charges between two localized states. Thus the decrease in dielectric constant after $x=0.2$ may be because of the fact that incorporation of Zn^{2+} ions consequently reduce the number of Fe^{3+} ions on B-sites which is mainly responsible for both space charge polarization and hopping exchange between two localized states. The initial increase in dielectric constant up to $x=0.2$ may be due to the formation of Fe^{3+} ions on octahedral sites.

3.4. Dielectric Loss

Figure 6 Shows the frequency dependence of dielectric loss in $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoferrites.

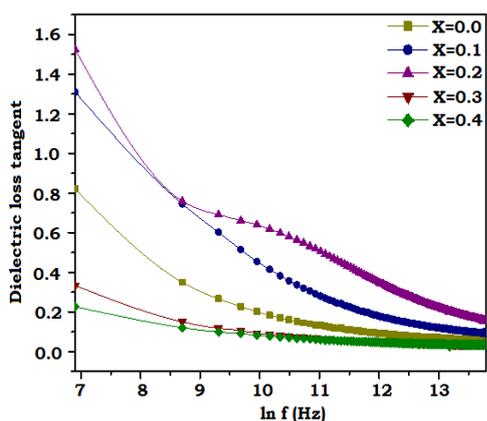


Figure 6. Variations of dielectric loss with frequency of $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoferrites

The decrease in dielectric loss tangent with increase in frequency is in accordance with the Koop's phenomenological model [23]. The dielectric loss arises if the polarization lags behind the applied alternating field and is caused by the presence of impurities and structural inhomogeneities. The value of dielectric loss tangent is very low in the present work indicating that the samples are structurally prefect.

Conclusion

Co-Zn ferrite nanoparticles were prepared successfully by solution combustion method. XRD results show the formation of single phase cubic spinel structure. The presence of Zn ions causes appreciable changes in the electrical and dielectric properties of CoFe_2O_4 . High value of dc resistivity, $10^8 \Omega \text{ cm}$, and very low values of the dielectric loss tangent are obtained in the present which shows that these ferrites are suitable for microwave applications.

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