Structural and electrical properties of neodymium substituted cobalt ferrite nanoparticles

S Xavier, S Thankachan, B P Jacob and E M Mohammed
Research Department of Physics, Maharaja’s College, Ernakulam, India
E-mail: emmohammed_2005@yahoo.com, sheena.xavier1@gmail.com

Abstract. A series of polycrystalline spinel ferrites with composition CoFe$_{2-x}$Nd$_x$O$_4$ (x=0.0, 0.05, 0.1, 0.15, 0.2, 0.25) have been synthesized by sol gel method. The structural characterizations of the prepared samples were done using XRD and TEM. The crystallite size shows an increase with the increase in the concentration of neodymium. The activation energy has been calculated from the temperature dependent DC conductivity measurements. The dielectric properties were studied and analyzed as a function of frequency. All the samples exhibit normal dielectric behaviour which is attributed to Maxwell–Wagner interfacial polarization.

1. Introduction
Polycrystalline ferrites are very good dielectric materials and has many technological applications ranging from microwave to radio frequencies [1]. Cobalt ferrite is an important member of ferrite family and is characterized by moderate saturation magnetization, high coercivity, mechanical hardness and chemical stability [2, 3]. The high electrical resistivity and good magnetic properties make this ferrite an excellent material for electronic and telecommunication applications.

The structural and electrical properties of cobalt ferrite are very sensitive to the method of preparation, the amount and the type of substitution [4]. The sol-gel technique is an excellent method to synthesize nanoparticles with maximum purity and narrow size distribution. It has been reported that partial substitution of Fe$^{3+}$ ions by rare earth in ferrite can modify its magnetic and electrical properties [5]. In the present study, structural and electrical properties of neodymium doped cobalt ferrite prepared by sol gel method have been presented.

2. Experimental methods
AR grade cobalt nitrate, neodymium nitrate and ferric nitrate were dissolved in ethylene glycol in the proper molar ratio using a magnetic stirrer. The solution was then heated at 60°C until a wet gel of the metal nitrates was obtained. The gel was dried at 120°C and finally self ignites to form a highly voluminous and fluffy powder. The obtained powder was ground well and sintered for 4 hours in a muffle furnace at 400°C. For electrical measurements, cylindrical disc-shaped pellets of the samples were made using a hydraulic press by applying a uniform pressure of 5 tons. The pellets were sintered at 500°C for 10 hours in a muffle furnace.

The neodymium doped cobalt ferrite samples were characterized by using X-ray powder diffractometer (Bruker AXS D8 Advance). The particle size was determined by subjecting the sample to Transmission Electron Microscopy. The DC conductivity studies were done using Keithley 6221.
DC current source and 2182A Nano volt meter. Dielectric measurements were carried out using precision impedance analyzer Wayne Kerr 6500B in the frequency range 20Hz to 30 MHz.

3. Results and discussion

3.1 X-ray diffraction analysis

The XRD pattern of CoFe$_{2-x}$Nd$_x$O$_4$ nanoparticles sintered at 400°C is depicted in figure 1. Comparing the XRD pattern with the standard data (ICDD file No. 22-1086), the formation of spinel phase in all the samples was confirmed.

![Figure 1. XRD pattern of CoFe$_{2-x}$Nd$_x$O$_4$.](image)

The crystallite size of the samples has been estimated from the broadening of XRD peaks using the Scherrer equation [4]. The crystallite sizes were increased by the gradual increasing in neodymium content and it is in agreement with the reported results [5]. The lattice parameter is calculated for prominent peak (311) using Bragg’s equation and the actual (X-ray) density were calculated. The bulk density was calculated from mass and bulk volume of the sample. Calculated values of lattice parameter, X-ray density, bulk density and porosity of all the samples are listed in table 1. The porosity of the samples was calculated from the X-ray density and bulk density.

| Nd content x | Lattice parameter(Å) | Crystallite Size (nm) | X-ray density (gcm$^{-3}$) | Bulk density (gcm$^{-3}$) | Porosity (%) |
|--------------|----------------------|-----------------------|---------------------------|--------------------------|--------------|
| 0.00         | 8.399                | 11.26                 | 5.260                     | 2.662                    | 48.96        |
| 0.05         | 8.422                | 13.00                 | 5.315                     | 2.716                    | 48.27        |
| 0.10         | 8.424                | 13.38                 | 5.408                     | 2.690                    | 50.23        |
| 0.15         | 8.425                | 14.04                 | 5.504                     | 2.581                    | 53.12        |
| 0.20         | 8.428                | 14.69                 | 5.598                     | 2.461                    | 56.02        |
| 0.25         | 8.432                | 17.64                 | 5.689                     | 2.665                    | 53.14        |

3.2 TEM analysis

The TEM images of the samples CoFe$_{2-x}$Nd$_x$O$_4$ (with x =0, 0.1) are shown in figures 2(a) and (b). In these figures, most of the particles appear with almost spherical shape and some are agglomerated. The particle size estimated from the different images of these samples lies in the range of 15 to 25 nm.
3.3 Electrical characterization

The temperature dependence of DC conductivity in cobalt ferrite is studied for different concentrations of neodymium and is shown in figure 3. The variation of conductivity with temperature shows the typical semiconducting nature of the ferrites. With the neodymium doping the DC conductivity of the samples varies from $1.698 \times 10^{-4}$ to $5.287 \times 10^{-5}$ S/m. According to the electron hopping model [2], the conductivity is mainly due to the hopping of electrons between Fe$^{2+}$ and Fe$^{3+}$ ions present at the octahedral B sites. The activation energy for conduction calculated from the Arrhenius plot is found to be very high (0.759eV), indicating the high resistive nature of the samples.

The variation of dielectric permittivity ($\varepsilon'$) with frequency is depicted in figure 4. It can be seen that dielectric permittivity exhibit an inverse dependence on frequency as reported for various ferrites. It decreases with frequency and remains a constant at higher frequencies. The decrease in permittivity with frequency can be explained on the basis of Koop’s theory [6] which considers the dielectric structure as an inhomogeneous medium of two layers of the Maxwell – Wagner type [7]. The space charge polarization occurring at the interfaces contribute to the enhanced $\varepsilon'$ values at lower frequencies. At higher frequencies, electron exchange between Fe$^{2+}$ and Fe$^{3+}$ ions will not be able to follow the applied electric field thus resulting in a decrease in polarization. When neodymium is doped in the system, it occupies the octahedral site in the ferrite system, decreasing the Fe$^{3+}$ ion number responsible for polarization. Hence the value of dielectric permittivity decreases with lower concentrations of neodymium content. However an increase in $\varepsilon'$ is noticed for higher neodymium content.
Figure 4. Variation of dielectric permittivity with frequency.

The variation of loss tangent with frequency for various neodymium concentrations is shown in figure 5. All the doped samples in the series exhibit relaxations at specific frequencies. Dielectric relaxation occurs when the hopping frequency of the charge carriers is approximately equal to that of external applied field [8].

Figure 5. Variation of dielectric loss (\(\tan \delta\)) with frequency.

4. Conclusions

Neodymium substituted cobalt ferrite nanoparticles were prepared successfully using the sol gel technique. The increase in crystallite size with the increase in the concentration of neodymium can be attributed to the large radii of the Nd\(^{3+}\) ions. The temperature variation of DC conductivity indicated the semiconducting behavior of the ferrites. The variation in the dielectric properties as a function of frequency and composition has been explained on the basis of Maxwell-Wagner theory of interfacial polarization. The high resistivity and low dielectric behavior make this ferrite useful in high frequency applications.

References

[1] Kharabe R G, Devan R S, Kanamadi C M and Chougule B K 2006 *Smart Mater. Struct.* **15** N36
[2] Veena G E, Al-Omari I A, Malini K A, Joy P A, Sakti K D, Yasuhiko Y and Anantharaman M R 2008 *J. Magn. Magn. Mater.* **321** 1092
[3] Cedeno – mattei Y and Perales-Perez O 2009 *Microelectronics Journal* **40** 673
[4] Gul I H, Abbasi A Z, Amin F, Anis-ur-Rehman M and Maqsood A 2007 *J. Magn. Magn. Mater.* **311** 494
[5] Binu P J, Smitha T, Sheena X and Mohammed E M 2011 *Physica Scripta* **84** 045702
[6] Koops C G 1951 *Phys. Rev.* **83** 121
[7] Wagner K W 1913 *Ann. Phys.* **40** 817
[8] Shigeki I and Toshio T 1971 *Japan. J. Appl. Phys.* **10** 260