Dielectric, Magnetic, Electric and Structural Properties of Ni$_{0.2}$-Co$_x$-Zn$_{0.8}$-X Ferrite Nanoparticles Synthesized By Sol-Gel Auto Combustion Method

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Abstract
Nickel substituted Co$_x$Zn$_{0.8}$-Fe$_2$O$_4$ (x=0.2, 0.5 and 0.6) ferrite were synthesized by Sol-gel auto combustion method. The powders were sintering at 400$^\circ$C and 700$^\circ$C for 2hrs to densify properly. The samples were characterized by XRD, SEM and FTIR and Magnetic properties. The XRD used to analyze phase structure and lattice parameters. The FTIR spectra confirm that synthesis material is ferrite. The crystalline, Structural, Resistivity, Dielectric, Sol-gel Auto Combustion method

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I. Introduction
Dielectric and Magnetic properties of Ni-Co-Zn have attracted attention because of their use at high frequency applications [1]. Because of high resistivity and low eddy current loss it also used as core material for transformer. NiFe$_2$O$_4$, CoFe$_2$O$_4$ and ZnFe$_2$O$_4$ shows good dielectric and magnetic properties for technical applications hence it is widely used in capacitor and magnetic cores of read-write heads for high speed digital recording and production of electronic and magnetic components [2], Which are depends on various parameters such as processing conditions, sintering temperature and time as well as on their chemical composition [3]. Researchers are used a variety of techniques including alternative sputtering technology, Pulse-Laser deposition, and spin-spray plating etc to deposit film [4]. However most of them cannot be economically applied on a large scale because they required high vacuum system, complicated experimental steps and high reaction temperatures. In this study, chemical synthesis route called sol-gel auto combustion method has been applied to synthesize NF, CF and ZF [5-11]. This method is useful to achieve the fabrication of magnetic nanoferrites at low annealing temperature. The size and morphology of nano particles and their properties may be controlled by modifying the composition of the nanocomposites and by thermal treatment conditions [8]. Due to the small size of the nanocrystals, an important part of the atoms are located at the surface this is the reason why the sol-gel synthesis method gone on intensive development [6]. Upto this stage the research work on Ni-CO-Zn ferrite is very limited. The sol-gel method was used for synthesis of this nanoferrites material. This method involves hydrolysis [7,8].

In this paper we present a study of the magnetic and structural properties of Ni$_{0.2}$CO$_{0.2}$Zn$_{0.6}$Fe$_2$O$_4$, Ni$_{0.2}$CO$_{0.5}$Zn$_{0.3}$Fe$_2$O$_4$ and Ni$_{0.2}$Co$_{0.8}$Zn$_{0.2}$Fe$_3$O$_4$ nanocomposites of different composition. The composition, crystal structure, morphology, and size distribution of Ni-Co-Zn ferrite nanocrystals can be controlled by adjusting the synthesis route and molar ratio of materials in the initial mixtures. The synthesized nano crystals have been characterized by XRD, SEM, FTIR, Dielectric and Magnetic Properties presented below are the details of investigation.
II. Experimental:
The Ni_{0.2}Co_{0.2}Zn_{0.6}Fe_{2}O_{4}, Ni_{0.2}Co_{0.2}Zn_{0.2}Fe_{2}O_{4}, and Ni_{0.2}Co_{0.2}Zn_{0.2}Fe_{2}O_{4} ferrite powders were prepared by co-precipitation and hydro thermal technique using iron nitrate, zinc nitrate, cobalt nitrate, and nickel nitrate as reaction agent. To obtain Ni_{0.2}Co_{0.2}Zn_{0.2}Fe_{2}O_{4}, Ni_{0.2}Co_{0.2}Zn_{0.2}Fe_{2}O_{4}, and Ni_{0.2}Co_{0.2}Zn_{0.2}Fe_{2}O_{4} ferrite powders, we have mixed AR grade iron nitrate, zinc nitrate, cobalt nitrate, and nickel nitrate with double distilled water. Citric acid was used as a chelating agent because it plays an important role in homogeneous mixture formation of metal cations. Reaction procedure was carried out in air atmosphere at room temperature. The composition was well shake and pH of solution is maintained as 7 by adding ammonia. The prepared solution was stirred on magnetic stirrer at low temperature 80°C to form a gel. The prepared ferrite samples were annealed for 400°C and 700°C. The general chemical reaction involves in synthetic process can be written as

\[(0.2)\text{Ni(NO}_3)_2.6\text{H}_2\text{O}+(x)\text{Co(NO}_3)_2.6\text{H}_2\text{O}+(x-0.8)\text{Zn (NO}_3)_2.6\text{H}_2\text{O}+2\text{Fe(NO}_3)_3.9\text{H}_2\text{O}+3\text{C}_2\text{H}_2\text{O} \rightarrow \text{Ni}_{0.2} \text{CO}_{x} \text{ZN}_{0.8} \text{Fe}_{2} \text{O}_4+4\text{N}_2↑+18\text{CO}_2↑+12\text{H}_2\text{O} \]

The synthesized nano crystalline samples were characterized by X-Ray Diffraction techniques at room temperature by using Philips powder X-Ray Diffractometer (model PW3710) with CuKα radiations having wavelength 1.5406 Å. The morphological behavior of the investigated samples was determined by using Scanning Electron Microscopy (SEM) techniques (model HITACHI Japan). Fourier Transform Infrared (FTIR) spectra were recorded in the range of 400-4000 cm\(^{-1}\) at room temperature by using Brukar Spectrometry and magnetic properties for Ni substituted nanocrystalline Ni_{0.2}Co_{0.2}Zn_{0.8}Fe_{2}O_{4} Spinal ferrite system sintered at 400°C and 700°C measured at room temperature with applied field of 6 KOe.

III. Result and Discussion:
3.1 X-Ray Diffraction.
To identify the possible formation of phase in Ni-Co-Zn ferrite an XRD analysis was done. The most intense peaks in all the specimens were found to match well with spherical spinel ferrite (JCPD). Lattice parameters and crystalline sizes of sintered ferrites specimens, evaluated by XRD analysis are shown in table (1) along with their composition, density, crystalline size, Porosity. There was a minor increase in lattice parameter which may be due to increasing concentration of Co and Zn. But lattice parameter increases with in increasing annealing temperature 400°C to 700°C. Decreasing densification may be due to the evolution of excess Co and Zn in the composition for Fe at room temp., 400°C and 700°C respectively. Decreasing in density may be due to vary with concentration of Co and Zn. Porosity is increases due to increasing temperature at room temp., 400°C and 700°C respectively. The XRD patterns are shown as in fig 1(a), (b), and (c).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature (°C)</th>
<th>Lattice Constant (a Å)</th>
<th>Inter planer Dist (d nm)</th>
<th>Density (Dx, gm/cc)</th>
<th>Porosity (% P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I] Ni(0.2)</td>
<td>Room</td>
<td>6.757</td>
<td>28.63</td>
<td>10.153x10(^6)</td>
<td>3.19</td>
</tr>
<tr>
<td>Co Zn</td>
<td>400</td>
<td>6.091</td>
<td>32.37</td>
<td>13.86x10(^6)</td>
<td>3.24</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>6.757</td>
<td>23.49</td>
<td>10.15x10(^6)</td>
<td>3.27</td>
</tr>
<tr>
<td>II] Ni(0.2)</td>
<td>Room</td>
<td>8.196</td>
<td>54.05</td>
<td>5.705x10(^6)</td>
<td>2.24</td>
</tr>
<tr>
<td>Co Zn</td>
<td>400</td>
<td>8.196</td>
<td>31.63</td>
<td>5.705x10(^6)</td>
<td>2.27</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>8.618</td>
<td>52.7</td>
<td>4.908x10(^6)</td>
<td>2.35</td>
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<tr>
<td>III] Ni(0.2)</td>
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<td>7.647</td>
<td>26.92</td>
<td>7.004x10(^6)</td>
<td>1.93</td>
</tr>
<tr>
<td>Co Zn</td>
<td>400</td>
<td>6.757</td>
<td>24.92</td>
<td>10.152x10(^6)</td>
<td>2.11</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>7.346</td>
<td>27.82</td>
<td>7.901x10(^6)</td>
<td>2.31</td>
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</table>
3.2 FT-IR Spectra:
In the present study Ni$_{0.2}$Co$_{0.2}$Zn$_{0.6}$Fe$_2$O$_4$, Ni$_{0.2}$Co$_{0.5}$Zn$_{0.3}$Fe$_2$O$_4$ and Ni$_{0.2}$Co$_{0.6}$Zn$_{0.2}$Fe$_2$O$_4$ ferrite has been synthesized at room temperature, 400$^\circ$C, and 700$^\circ$C. The synthesis process is carried out using sol-gel auto combustion method. The citric acid was used a reducing agent in reaction. The of Ni$_{0.2}$Co$_{0.2}$Zn$_{0.6}$Fe$_2$O$_4$ IR curve fig 2(a) of sintered powder shows strong absorption band 1619.912 Cm$^{-1}$ to 2339 Cm$^{-1}$ indicates N-H Bending structure, the strong absorption band at 2341.15 Cm$^{-1}$ indicating C triple bond N- Stretched. The band at 1715.46 Cm$^{-1}$ indicating C-H out of plane bending carbohydrates which is very weak and shifted to low frequency.
The of Ni$_{0.2}$CO$_{0.5}$Zn$_{0.3}$Fe$_2$O$_4$ IR curve fig2(b) of sintered powder shows strong absorption band 1345.10 Cm$^{-1}$ to 1629.55 Cm$^{-1}$ indicates N-H Bending structure, the strong absorption band at 2341.15 Cm$^{-1}$ indicating C triple bond N- Stretched. The band at 668.21 Cm$^{-1}$ indicating C-H out of plane bending carbohydrates which is very weak and shifted to low frequency.

The of Ni$_{0.2}$CO$_{0.6}$Zn$_{0.2}$Fe$_2$O$_4$ IR curve fig2(c) of sintered powder shows strong absorption band 14825.027 Cm$^{-1}$ to 1627.62 Cm$^{-1}$ indicates N-H Bending structure, the strong absorption band at 2341.15 Cm$^{-1}$ indicating C triple bond N- Stretched. The band at 714.49 Cm$^{-1}$ indicating C-H out of plane bending carbohydrates which is very weak and shifted to low frequency.
3.3 SEM Morphology:

Performing SEM we analyzed the structure of Ni$_{0.6}$CO$_{0.2}$Zn$_{0.2}$Fe$_2$O$_4$, Ni$_{0.2}$CO$_{0.5}$Zn$_{0.3}$Fe$_2$O$_4$ and Ni$_{0.2}$CO$_{0.6}$Zn$_{0.2}$Fe$_2$O$_4$ shows typical morphology in fig3(a,b,c). For samples synthesized by sol-gel method the surface has compact structure with smallest particle size typically less than 60 nm. The micrograph of samples sintered at 400°C and 700°C indicating that microstructure is completely form these temperature. The grain size increases with increase in temperature.

Fig-3(a) SEM Morphology of Sintered Ni$_{0.2}$CO$_{0.2}$Zn$_{0.2}$Fe$_2$O$_4$ Ferrites.

Fig-3(b) SEM Morphology of Sintered Ni$_{0.2}$CO$_{0.5}$Zn$_{0.3}$Fe$_2$O$_4$ Ferrites.

Fig-3(c) SEM Morphology of Sintered Ni$_{0.2}$CO$_{0.6}$Zn$_{0.2}$Fe$_2$O$_4$ Ferrites.
3.4 Magnetic Properties:

Hysteresis loops of synthesized sample are shown in Fig. 4. Saturation magnetization value is 2.3 emu/g for the sample sintered at 700°C and the same is 0.5 emu/g for the sample sintered at 400°C. The increase of saturation magnetization with the increase in sintering temperature is an indication that the average magnetic domain size of the particle is increasing and the atomic spins are getting more and more aligned with the direction of the applied magnetic field. The increase in coercivity can result from an increase in particle size from super paramagnetic size to single domain size, the effect of surface anisotropy and thermal energies.

3.5 Dielectric properties:

The variation of dielectric constant with temperature versus frequency is studied and depicted in the Fig. 5. It is clear that dielectric constant increases with temperature at all frequencies. It also show the variation in the dielectric loss factor of Ni-Co-Zn ferrite sintered at various temperatures. The decrease takes place when the jumping frequencies of electric charge carriers cannot follow the alteration of applied AC electric field beyond a certain critical frequencies.

3.6 Resistivity

Sintered ferrite (Ni0.2Co0.2Zn0.6)Fe2O4 composition is optimize and pellet specimens were used to determine resistivity. Electrodes were painted on the surface of the sample using a conducting silver paste followed by curing at 300°C for 1/2 h. The AC resistivity \( \rho \) was analyzed by Impedance Analyzer Model 4192A, Hewlett Packard, USA. The Ferrite (Ni0.2Co0.2Zn0.6)Fe2O4 shows the resistivity of about 9.2 MΩ·cm at 100 kHz with frequency stability up to \( \sim \)10 MHz. The improved resistive properties of the composition might be due to the lowering of magnetostriction constant by Ni and Co-Zn substitution and partly due to better densification. Due to different concentration of Zn and Co at constant Ni shows increase in interplaner distance for normal temperature to 400°C and again decrease for 400°C to 700°C.

VI. Conclusion:

The Ni-Co-Zn spinel ferrite nanoparticles were successfully synthesized by sol-gel auto combustion method. By varying the concentration of CoFe2O4 (CF), and ZnFe2O4 (ZF) at constant Ni Fe2O4 (NF), there is increase in Lattice Constant, Inter planer distance, Porosity and decrease in Density at increasing temperature. The FTIR investigation shows strong absorption of Co and Zn ions. The nano crystalline natures confirm from...
SEM and XRD. SEM shows spherical spinel structure. XRD pattern confirm the formation of spherical spinel phase. The lattice parameters, Porosity and Density of ferrite materials are changes for different concentration and different temperature. The increase of saturation magnetization with the increase in sintering temperature is an indication that the average magnetic domain size of the particle is increasing and the atomic spins are getting more and more aligned with the direction of the applied magnetic field. The improved resistive properties of the composition might be due to the lowering of magnetostriction constant by Ni and Co-Zn substitution and partly due to better densification. The rapid increase in the dielectric constant with temperature at low frequencies suggests that the effect of temperature is more pronounced on the interfacial polarization than on the dipolar polarization. Therefore a constant and low value of the dielectric constant at high frequencies is observed.

References: