Electrical and structural properties of zinc substituted nickel ferrites synthesized by sol-gel technique

Sunita Khangembam, Maisnam Victory, Waikhom Surchandra, Sumitra Phanjoubam*

Department of Physics, Manipur University, Manipur, Canchipur, 795003, India

*Corresponding author, E-mail: sumitraphanjoubam@gmail.com; Tel: (+91) 9436894642

Received: 31 March 2016, Revised: 26 September 2016 and Accepted: 20 December 2016

DOI: 10.5185/amp.2017/306
www.vbripress.com/amp

Abstract

Recent technological breakthroughs and the desire for new functions generate an enormous demand for synthesizing new materials through different ways and methods which show superior properties compared with their pure counterparts. Presently, polycrystalline zinc doped nickel ferrites having the compositional formula Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ where $x = 0.0, 0.1, 0.2$ and $0.4$ were synthesized. Sol-gel auto combustion method was adopted for the preparation of these ferrites since it provides a simple and economic alternative technique ensuring good stoichiometric control, production of particles with narrow size distribution in a relatively shorter time, good homogeneity and high sinterability at lower temperature. Structural studies were carried out by XRD. Various structural properties like lattice parameter, crystallite size and density were calculated from the XRD data. Micro structural studies were carried out using Scanning Electron Microscopy (SEM), while the elemental compositions of all the samples were studied by Energy Dispersive X-ray Analysis (EDAX). The frequency variation of room temperature dielectric constant and dielectric loss was studied in the frequency range $100$Hz – $1$MHz and dispersive behavior was observed. The room temperature dc resistivity of all the samples was also investigated. Zn substituted nickel ferrites are found to be useful in microwave and electronic devices. Copyright © 2017 VBRI Press.

Keywords: Ni ferrite, sol-gel, XRD, SEM, dielectric.

Introduction

Ferrites with spinel structure are technologically important class of magnetic materials with Fe$_2$O$_3$ as their main component having the general formula MFe$_2$O$_4$ where M represents metallic cation like Zn$^{2+}$, Co$^{2+}$, Mg$^{2+}$, Mn$^{2+}$ etc. This class of materials bridges scientific discipline and combines the best attribute of the different world in one system. Recent investigations show many interesting properties of ferrites which are largely dependent upon the synthesis technique, nature of dopant, dopant concentration and heating conditions. Its property of versatility gives rise to a number of different types of ferrites with varied properties. Nickel ferrites have inverse spinel structure i.e. oxygen ions have cubic closed packing arrangement where Ni exhibits a strong octahedral site preference. Nickel and substituted nickel ferrites play significant role in technological applications such as microwave devices, power transformer in electronics, rod antenna, read/write heads for high speed digital tapes etc because of their high resistivity, low dielectric loss and high Curie temperature etc [1-5].

Among the various substituted nickel ferrites, NiZn ferrites are one of the most versatile soft magnetic materials. NiZn ferrite is a mixed spinel ferrite in which A – sites (tetrahedral sites) are occupied by Zn$^{2+}$ and Fe$^{3+}$, B – sites (octahedral sites) are occupied by Ni$^{2+}$ and Fe$^{3+}$ ions. The compositional variation in these ferrites results in the redistribution of metal ions over the tetrahedral and octahedral sites which can modify their properties. Besides substitution, synthesis methods also greatly influence the properties of these ferrites [6-9]. Employment of chemical methods like sol-gel, co-precipitation, spray drying, citrate precursor, and hydrothermal methods other than the conventional ceramic method provides a simple and economic alternative, high degree of compositional homogeneity content in relatively short processing time at a very low temperature for preparation of ferrites with enhanced properties [10-13]. This paper focuses on the preparation of Zn substituted Ni ferrites by sol-gel technique with an aim to investigate the effect of substitution level on the structural, micro structural and electrical properties of the samples.

Experimental

Materials
The starting materials for the synthesis of zinc doped nickel ferrites include hexydrated zinc nitrate (Zn(NO$_3$)$_2$.6H$_2$O purity~96%) from Merck, Mumbai, hexydrated nickel nitrate (Ni(NO$_3$)$_2$.6H$_2$O, purity~97%) from Merck, Mumbai, nanohydrated iron nitrate (Fe(NO$_3$)$_2$.9H$_2$O, purity~98%) from Merck, Mumbai. The polyvinyl alcohol 1 (PVA) polymer powder from LOBA Chemie, Mumbai, the ethanediol (ethylene glycol) (CH$_2$OH).CH$_2$OH, purity~99%) from S.d. fine CHEM PVT.LTD., BOISAR and all the chemicals are used without further purification. The deionised (DI) water is used as solvent.

**Materials synthesis**

For the preparation of polycrystalline nickel ferrites having compositional formula Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ where $x$ = 0.0, 0.1, 0.2 and 0.4 employing sol-gel autocombustion technique stoichiometric ratios of Ni(NO$_3$)$_2$.6H$_2$O, Zn(NO$_3$)$_2$.6H$_2$O and Fe(NO$_3$)$_2$.9H$_2$O are taken and dissolved in ethylene glycol in the ratio 3:1 to obtain the precursor solutions. The obtained precursor solution is then heated at 40°C with constant stirring until a clear solution is obtained. The temperature is increased to 60°C and finally to 100°C till the solution starts to burn with the release of a lot of heat producing a highly voluminous fluffy product. The product so obtained is the as prepared nickel zinc ferrite powder. The obtained powder samples are pre-sintered at 700°C for 3 hours. This powder is then ground and mixed with 3 wt. % of PVA which acts as a binder and then pressed into pellets with 100kg/cm$^3$ pressure for 5 mins. These pellets are finally sintered at 1000°C for 5 hours which are then used for various structural and electrical measurements.

**Characterizations**

The single phase formation of the samples was confirmed by X-ray diffraction studies using a Philips X’pert Pro Pan Analytic XRD using CuK$\alpha$ radiation of wavelength $\lambda$ = 1.5406Å, by varying angle (2θ) from 20° to 80°. The lattice parameter ($a$) was calculated from the XRD data using the formula,

$$\text{\(d \approx a/(h^2 + k^2 + l^2)^{1/2}\)}$$  \hspace{1cm} (1)

where, ‘d’ is the interplanar spacing and (h k l) the miller indices. The crystallite size ($D$) was determined from the XRD data using the Debye-Scherer’s formula,

$$\text{\(D = 0.94\lambda/\beta\cos\theta\)}$$  \hspace{1cm} (2)

where, $\lambda$ is the wavelength of Cu target ($\lambda$=15.406nm), $\beta$ the full width at half maximum and $\theta$ the Bragg’s diffraction angle. The X-ray density ($d_x$) was calculated using the formula,

$$\text{\(d_x = 8M/N\alpha^3\)}$$  \hspace{1cm} (3)

where, ‘M’ is the molecular mass and ‘N’ the Avogadro’s number. The microstructure of the samples was recorded using Scanning Electron Microscope (SEM FEI QUANTA-250), while the elemental compositions of all the samples were studied by Energy Dispersive X-ray Analysis (EDAX). Electrical contacts were made on both sides of the flat surfaces of each pellet using silver coatings for ohmic contact. Dielectric measurements were done on these pellets using Agilent HP 4284 A LCR meter as a function of frequency in the range 100Hz to 1MHz. The corresponding loss tangent, tanδ, was also simultaneously recorded. The room temperature resistance of each composition was measured using a multimeter. From the observed value of R, the room temperature dc resistivity ($\rho$) was evaluated using the formulas. $\rho$ =RA/d where A is the area and d the thickness of the sample.

**Results and discussion**

**X-ray diffraction analysis**

The typical XRD pattern for Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ samples for $x$ = 0.0, 0.1, 0.2 and 0.4 are depicted in Fig. 1 showing main intensity peaks corresponding to specific planes (220), (311), (400), (422), (511) and (440) without any extra lines which confirms the single phase spinel structure of all the samples planes.

![Fig. 1. XRD pattern for Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrites for x = a) 0.0, b) 0.1 c) 0.2 and d) 0.4.](image)

Various structural properties like lattice parameter and crystallite size are calculated from the XRD data and are listed in Table 1.

<table>
<thead>
<tr>
<th>Composition $x$</th>
<th>Lattice parameter ‘a’ (Å)</th>
<th>Crystallite size ‘D’ (nm)</th>
<th>Theoretical density ‘d$_c$’ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.325</td>
<td>171.90</td>
<td>5.40</td>
</tr>
<tr>
<td>0.1</td>
<td>8.344</td>
<td>163.43</td>
<td>5.34</td>
</tr>
<tr>
<td>0.2</td>
<td>8.347</td>
<td>128.39</td>
<td>5.38</td>
</tr>
<tr>
<td>0.4</td>
<td>8.354</td>
<td>143.69</td>
<td>5.36</td>
</tr>
</tbody>
</table>
It is observed that the lattice parameter increases with the increase of Zn\(^{2+}\) content. This can be attributed to the fact that Ni\(^{2+}\) ions with ionic radii 0.78 Å have been replaced by Zn\(^{2+}\) ions of larger ionic radius 0.82 Å. Since larger ions are replacing the smaller ones, an increase in the lattice parameter is expected [14]. The crystallite size was found to decrease with the increase of Zn\(^{2+}\) content.

**SEM and EDAX analysis**

Fig. 2 shows the SEM photomicrographs for Ni\(_{1-x}\)Zn\(_{x}\)Fe\(_2\)O\(_4\) samples for x = 0.0, 0.1, 0.2 and 0.4, depicting well defined grains. The average grain size of the samples was found to be in the range 350-500 nm. These samples prepared by the chemical method showed grain size which is much reduced from that of ferrites prepared by conventional ceramic method (~ order of micrometer) [15].

![SEM photomicrographs for Ni\(_{1-x}\)Zn\(_{x}\)Fe\(_2\)O\(_4\) ferrites](image)

**Dielectric properties study**

The dependence of dielectric constant of Ni-Zn ferrites as a function of frequency in the range 100 Hz - 1 MHz as observed in Fig. 4 shows a dispersive behavior. This behavior can be explained in terms of Maxwell-Wagner type of interfacial polarization in accordance with Koop’s phenomenological theory [16-18]. It is well known that ferrites are composed of well-defined grains and separated by grain boundaries. The grains are known to be conducting while the grain boundaries are highly resistive. The main mode of conduction in ferrites is the electron hopping between ions of the same element present in more than one valency state at crystallographic equivalent lattice sites and this is commonly termed as Verwey mechanism of electron hopping [19].

![Variation of dielectric constant with frequency](image)

**Table 2. Elemental percentage in Ni\(_{1-x}\)Zn\(_{x}\)Fe\(_2\)O\(_4\) ferrites.**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ni(^{2+}) (%)</th>
<th>Zn(^{2+}) (%)</th>
<th>Fe(^{3+}) (%)</th>
<th>O(^{2-}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>12.73</td>
<td>0.00</td>
<td>28.89</td>
<td>58.38</td>
</tr>
<tr>
<td>0.1</td>
<td>10.97</td>
<td>1.28</td>
<td>27.74</td>
<td>60.00</td>
</tr>
<tr>
<td>0.2</td>
<td>10.76</td>
<td>2.68</td>
<td>29.92</td>
<td>56.65</td>
</tr>
<tr>
<td>0.4</td>
<td>9.76</td>
<td>4.33</td>
<td>32.51</td>
<td>53.39</td>
</tr>
</tbody>
</table>

The study of energy dispersive analysis of X-ray of the samples confirms the chemical composition and stoichiometric proportions. The typical EDAX spectra for x=0.2 is shown in Fig. 3 and the compositional percentage of Zn\(^{2+}\), Ni\(^{2+}\), Fe\(^{3+}\) and O\(^{2-}\) is listed in Table 2. Existence of impurity phase has not been observed. The ions present in Ni\(_{1-x}\)Zn\(_{x}\)Fe\(_2\)O\(_4\) where x = 0.0, 0.1, 0.2 and 0.4 are observed to be in stoichiometric proportions.

![EDAX spectra of Ni\(_{1-x}\)Zn\(_{x}\)Fe\(_2\)O\(_4\) ferrites (x=0.2)](image)
grain boundaries block the mobile charge carriers and inhibit charge migration leading to piling up of charges at the grain boundary thereby causing polarization [16-18, 20]. At low frequencies of an applied field, a net oscillation of charges between barriers occurs producing a very large capacitance and hence a large dielectric constant [20], as has been observed. As the frequency of the applied field increases, the electrons reverse their direction of motion more often which decreases the probability of electrons reaching the grain boundary and as a result the polarization decreases [21]. Hence, the observed decrease in the dielectric constant (shown in Fig. 4). At much higher frequencies of the applied field, the electronic hopping could not follow the frequencies of the alternating field, and therefore a low and nearly constant value of the dielectric constant is expected [22], and has been obtained.

The variation of dielectric loss (tanδ) as a function of frequency in the range 100Hz -1MHz is depicted in Fig. 5. It can be seen that the loss tangent decrease continuously with increasing frequency. None of the samples exhibit loss peak. The decrease of tanδ with frequency can be explained in accordance with Koop’s phenomenological model [17] as discussed above. As the frequency of the applied electric field increases, the hopping frequency of the charge carrier cannot follow the alternating field and become independent of it and as a result the value of tanδ decreases [23, 24].

![Dielectric loss vs Frequency](image)

**Fig. 5.** Variation of dielectric loss with frequency.

**DC resistivity measurement**

The variation of room temperature DC resistivity with Zn²⁺ substitution is shown in Fig. 6. It is observed that the value of DC resistivity decreases with the increase of Zn²⁺ content. Resistivity in ferrites is explained by the electron hopping mechanism between Fe²⁺ and Fe³⁺ ions at B-site. The decrease in resistivity may be understood in terms of the substitution of Zn²⁺ ions and the cation distribution. Zn²⁺ prefer to occupy the tetrahedral A site, Ni³⁺ the octahedral B site, while Fe³⁺ ions partially occupy A and B sites. The cation distribution may be assumed as (ZnₓFe₁₋ₓ)₃[NiₓFe₂₋ₓ] [24]. On increasing Zn²⁺ concentration at A sites, Ni³⁺ concentration at B sites will decrease. This leads to migration of some Fe³⁺ ions from A site to B site to balance the reduction in Ni³⁺ ions concentration at B sites. The Fe³⁺ ions that may have been formed has B-site preference. As a result, the number of Fe³⁺ and Fe²⁺ ions at B sites which are responsible for electrical conductivity in ferrites increase and consequently resistivity decreases [25-27].

![DC Resistivity vs Zn content](image)

**Fig. 6.** Variation of DC resistivity with Zn content.

**Conclusion**

A series of Zn substituted Ni-ferrites were successfully synthesized by chemical sol-gel method. X-ray diffraction confirmed the formation of single phase spinel structure of all the samples. Lattice parameter and crystallite size were calculated from the XRD data. The dielectric constant and loss decrease with the increase of frequency and attains constant value as the frequency increases. The value of DC resistivity decreases with the increase of Zn substitution.

**Acknowledgements**

The authors would like to acknowledge the XRD and SEM Central Facilities of Manipur University.

**References**