Analysis of Dielectric and Resistive Properties of Sn Substitution in Ni-Zn Ferrites Nanoparticles

Arif Mahmud*

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Abstract

Ni-Zn Ferrites samples were prepared by solid state reaction method by introducing Sn. Polycrystalline samples were molded following this combination $\text{Ni}_{0.6-0.25}\text{Zn}_{0.4-0.25}\text{Sn}_{x}\text{Fe}_{2}\text{O}_{4}$ ($0 \leq x \leq 0.2$) and sintered at temperature 1325°C for 180 minutes. The structural, magnetic and transport properties of various ferrite samples were studied with the Sn substitution. XRD patterns indicate that the synthesized ferrite compositions were of single phase cubic spinel without any trace of impurity. Lattice parameter of the samples was found to decrease with increasing Sn concentration in the system obeying Vegard’s law. Dielectric constant decreased with the increase of frequency which is rapid at lower and slower at higher frequencies. This is a normal dielectric behavior in most of the ferromagnetic materials, which follow Maxwell and Wagner prediction. With the increase of temperature, dielectric constant and dielectric loss tangent are observed to be increased. The AC electrical resistivity, measured as a function of temperature, decreases with the increase of temperature indicating the semiconducting nature of all the samples. The activation energy of the all samples were calculated from the plot of $\ln(\rho/\rho_0)$ vs. $1/T$ curve. The lower activation energies are associated with higher electrical conductivity.

Keywords: Ferrites; Electrical Properties; X-ray Diffraction; Temperature and Resistivity

1. Introduction

Spinel ferrites are natural super lattice according to their structure. Ni-Zn ferrites with the spinel crystal structure are being extensively used in a number of electronic devices because of remarkably high electrical resistivity, low magnetic coercivity, mechanical hardness, chemical stability and reasonable cost. Due to their remarkable behavior of magnetic and electric properties
they are subjects of intense theoretical and experimental investigation for application purpose. Low electrical resistivity makes iron and soft magnetic alloys technologically useless for applications at high frequencies. The problem is that their low electrical resistivity allows eddy currents to flow within the materials themselves, thereby producing heat. This wasted energy or the produced heat often causes a serious problem. Thus, non-ferrite materials become inefficient and spinel oxides have been the subject of great interest because of their wide applications in the high frequency devices (Ruiz et al., 2013). Spinel ferrite plays an important role in different technical fields such as telecommunication, AC and DC motors, power distribution transformers, communication systems, digital memories, multilayer chip inductors, radar and satellite communications and in many other technological applications like photoelectrical devices, particle accelerators and gas sensors, magneto-mechanical stress and torque sensors, microwave devices and biomedical applications (Pasquale et al., 2002). Wastage of electromagnetic energy (heat) is known as dielectric loss. It is also known as dielectric absorption and represented by tanδ. The study of dielectric properties provides valuable information on the behavior of localized electric charge carriers leading to greater understanding of the mechanism of dielectric polarization in ferrite system. Especially ferrites are convenient for high frequency uses because of their high resistivity. The electrical conductivity and dielectric behavior of ferrites are strongly depended on the sintering time and temperature, chemical composition, preparation conditions. Extensive work has been done on electrical conductivity of different ferrite samples with varying compositions have been investigated by different workers (Hoque et al., 2002; Gul et al., 2007). It has been reported that by incorporating small amount of tetravalent tin additive, the electrical and micro structural properties of Ni-Zn ferrites are significantly influenced. The main objectives of this present research work was to prepare various samples of ferrites inducing Sn i.e. \( \text{Ni}_{0.6-x/2}\text{Zn}_{0.4-x/2}\text{Sn}_x\text{Fe}_2\text{O}_4 \) \( (x=0, 0.05, 0.1, 0.15 \) and \( 0.2) \) to analyze the structural, electric and resistive properties of various ferrite samples by solid state reaction method (Patil et al., 2009).

2. Materials and Methods

Ferrite samples of \( \text{Ni}_{0.6-x/2}\text{Zn}_{0.4-x/2}\text{Sn}_x\text{Fe}_2\text{O}_4 \) were prepared using Conventional Ceramic Process or Solid State Reaction Method and sintered at temperature 1325°C for three hours with different compositions. The raw materials for the preparation of Ni-Zn ferrites were oxides of iron, Nickel and Zinc. The constituent required in stoichiometric proportions were weighed first and then thoroughly mixed using ceramic mortar and resultant powder was then ball milled 3 hours in distilled water to produce a homogeneous mixture of the constituents. Then the mixtures are calcined in air or oxygen at a temperature above 1000°C. For some time, this process is continued until the mixture is converted into the correct crystalline phase. Sintering is carried out in the solid state, at temperature ranging 1100-1400°C, for times of typically 1-4 h and in various atmospheres (e.g. Air, \( \text{O}_2 \) and \( \text{N}_2 \)). Therefore prepared slurry were dried, palletized and then transferred to a porcelain crucible for pre-firing at temperature 950°C and was performed in Gallen Camp furnace available at the Materials Science Division, Atomic Energy Center, Dhaka, Bangladesh. The
properties of Ni–Zn samples are influenced considerably by sintering temperature and compositions.

X-ray diffraction was carried out with an X-ray diffractometer for the samples Ni$_{0.6-x/2}$Zn$_{0.4-x/2}$Sn$_x$Fe$_2$O$_4$ with different concentration of $x$. Resistivity of the samples has been measured using conventional two probe method, using pellet samples of 7.24mm–7.61mm diameter and 1.12mm–1.41mm thickness. The two probe method is one of the standards and most commonly used method for the measurement of resistivity of very high resistivity sample. Dielectric Constants were measured using Hewlett Packart impedance analyzer as a function of frequency in the range 1 kHz - 13 MHz at room temperature.

3. Result and Discussion

3.1 X-ray Diffraction

Structural characterization and diffraction is a prior for the study of ferrite properties. Optimum electric properties of the ferrites necessitate having single phase cubic structure. X-ray diffraction is useful technique to evaluate the various phases of the synthesized ferrites as well as their unit cells parameters. In the present study X-ray diffraction technique has been utilized to discern these parameters. The X-ray diffraction (XRD) patterns for the samples Ni$_{0.6-x/2}$Zn$_{0.4-x/2}$Sn$_x$Fe$_2$O$_4$ are shown in Fig. 1.

![X-ray diffraction patterns for Ni$_{0.6-x/2}$Zn$_{0.4-x/2}$Sn$_x$Fe$_2$O$_4$ with $x$ = 0, 0.05, 0.1, 0.15 and 0.2.](image)

The fundamental reflections from the planes of (111), (220), (311), (222), (400), (422), (333) and (440) characterizing the cubic spinel structures are observed for $x$=0, 0.05, 0.1, 0.15, 0.2. This represents that the synthesized ferrite compositions are of single phase cubic spinel. Investigated samples demonstrate the homogeneity. Analyzing the XRD patterns, we find that the intensity is maximum for plane (311) at the position 35.5 of miller indices.
For x=0.2, the Sn ion induces a foreign phase which can suggest a solubility limit of Sn\(^{4+}\) ions in the spinel lattice due to its radius (Huheey et al., 1993). The positions of the peaks and their corresponding miller indices for the studied samples investigated are given in Table 1. The values of lattice parameter “a” corresponding to all peaks plotted against Nelson–Riley function, F(θ) for an accurate determination of lattice parameter. Fig. 2 shows the representative curves for Sn content of extrapolating N-R function. The least square linear fitting gives the precise lattice parameter as an intercept on the Y-axis. The measured lattice parameter, density and porosity for different samples are given in Table 2. The theoretical density \(\rho_{th}\) was calculated using following expression:

\[
\rho_{th} = \frac{8M}{N_A a^3} \rho / cm^3
\]

Where \(N_A\) is Avogadro’s number \((6.02 \times 10^{23} \text{ mol}^{-1})\), M is the molecular weight. The porosity was calculated from the relation \(100(\rho_{th} - \rho_B) / \rho_{th}\)\%, where \(\rho_B\) is the bulk density measured by the formula, \(\rho_B = M / V\). Fig. 3 shows the variation of lattice constant with increase in Sn concentration. From this we can see that with the increase of Sn content lattice parameters are increasing linearly, which represent the variation of tetrahedral radius with increase in Sn concentration, calculated by the following equation:

\[
r_{tet} = (1-X) r_{tet,Fe}^{3+} + (X) r_{tet,Sn}^{4+}
\]

Table 1 X-ray peak positions for Ni\(_{0.6-x/2}\)Zn\(_{0.4-x/2}\)Sn\(_{x}\)Fe\(_2\)O\(_4\) samples.

<table>
<thead>
<tr>
<th>Composition</th>
<th>X-ray peak position with Miller indices 2θ (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(<em>{0.6})Zn(</em>{0.4})Fe(_2)O(_4)</td>
<td>(111) 18.37 30.19 35.5 37.17 43.19 53.57 57.11 62.71</td>
</tr>
<tr>
<td>Ni(<em>{0.575})Zn(</em>{0.375})Sn(_{0.05})Fe(_2)O(_4)</td>
<td>(111) 18.33 30.15 35.51 37.19 43.17 53.51 57.05 62.65</td>
</tr>
<tr>
<td>Ni(<em>{0.55})Zn(</em>{0.35})Sn(_{0.1})Fe(_2)O(_4)</td>
<td>(111) 18.33 30.17 35.53 37.17 43.17 53.55 57.09 62.71</td>
</tr>
<tr>
<td>Ni(<em>{0.525})Zn(</em>{0.325})Sn(_{0.15})Fe(_2)O(_4)</td>
<td>(111) 18.33 30.15 35.51 37.13 43.17 53.53 57.05 62.67</td>
</tr>
<tr>
<td>Ni(<em>{0.5})Zn(</em>{0.3})Sn(_{0.2})Fe(_2)O(_4)</td>
<td>(111) 18.29 30.69 35.45 37.65 43.09 53.43 56.95 62.53</td>
</tr>
</tbody>
</table>

Table 2 The lattice parameter, theoretical and bulk density and porosity of the Ni\(_{0.6-x/2}\)Zn\(_{0.4-x/2}\)Sn\(_x\)Fe\(_2\)O\(_4\) samples.

<table>
<thead>
<tr>
<th>Sample Composition</th>
<th>(a_0) (Å)</th>
<th>(\rho_{th}) (gm/cm(^3))</th>
<th>(\rho_B) (gm/cm(^3))</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(<em>{0.6})Zn(</em>{0.4})Fe(_2)O(_4)</td>
<td>8.535791</td>
<td>5.06</td>
<td>4.23</td>
<td>16.4</td>
</tr>
<tr>
<td>Ni(<em>{0.575})Zn(</em>{0.375})Sn(_{0.05})Fe(_2)O(_4)</td>
<td>8.54717</td>
<td>4.98</td>
<td>4.32</td>
<td>13.2</td>
</tr>
<tr>
<td>Ni(<em>{0.55})Zn(</em>{0.35})Sn(_{0.1})Fe(_2)O(_4)</td>
<td>8.544105</td>
<td>5.27</td>
<td>4.78</td>
<td>9.2</td>
</tr>
<tr>
<td>Ni(<em>{0.525})Zn(</em>{0.325})Sn(_{0.15})Fe(_2)O(_4)</td>
<td>8.548157</td>
<td>5.82</td>
<td>5.37</td>
<td>7.7</td>
</tr>
<tr>
<td>Ni(<em>{0.5})Zn(</em>{0.3})Sn(_{0.2})Fe(_2)O(_4)</td>
<td>8.564141</td>
<td>5.55</td>
<td>5.14</td>
<td>7.3</td>
</tr>
</tbody>
</table>
The variation of lattice constant ‘a’ with Nelson-Riley function for all the samples.

The lattice parameter of SnFe₂O₄ varies between the values 8.53Å – 8.56Å and in ferrites; Ni²⁺ and Sn⁴⁺ are preferred in the octahedral sites of oxygen lattice. The ionic radii of Ni²⁺, Zn²⁺, Sn⁴⁺ in octahedral sites are 0.69Å, 0.74Å and 0.83Å respectively and obey (O’Neill et al., 1992). When a cation whose radius and valence are different from those of the host cations is introduced into the spinel lattice, the ionic size mismatch between the host and dopant cations creates a strain in the lattice which can affect the unit cell size. Hence it is expected that the lattice parameter of the Ni-Zn-Sn ferrite would increase with the increase of Sn content in the spinel. In Fig. 3, the plot of the lattice parameter obtained from different composition of Ni, Zn, and Sn is shown. It is well known that the distribution of cations in the octahedral B-sites and tetrahedral A-sites determines to a great extent the physical, electrical and magnetic properties of ferrites. There exists a correlation between the ionic radius and the lattice constant, the increase of the lattice constant is proportional to the increase of the ionic radius. The experimental values of lattice parameter follow
the Vegard’s rule of linearity (Vegard, 1921). Thus the introduction of larger ions in the ferrite lattice results in an increase of the distance between the magnetic ions which facilitates the possibility of studying fundamental properties like Curie temperature and magnetization as affected by distance dependence exchange interaction. In general, a cation disorder develops in SnFe$_2$O$_4$ when it is prepared by solid state method. It was reported that around 10% of Sn$^{4+}$ was distributed in tetrahedral sites of the spinel during synthesis. Such disorder of Sn$^{4+}$ might be the reason for the variation of lattice parameters of various Sn ferrites by different investigators (Allen et al., 1988).

![Lattice parameters calculated from X-ray diffraction patterns plotted as a function of Sn content in the series Ni$_{0.6-x/2}$Zn$_{0.4-x/2}$Sn$_x$Fe$_2$O$_4$.](image)

**Fig. 3.** Lattice parameters calculated from X-ray diffraction patterns plotted as a function of Sn content in the series Ni$_{0.6-x/2}$Zn$_{0.4-x/2}$Sn$_x$Fe$_2$O$_4$.

![Variation of density with increase of Sn content.](image)

**Fig. 4 (a).** Variation of density with increase of Sn content.

![Variation of porosity with the increase of Sn content.](image)

**Fig. 4 (b).** Variation of porosity with the increase of Sn content.

Density of ferrite samples plays a vital role in the determination of magnetic as well as electrical properties. It is well known that high permeability could be achieved by increasing the density of ferrites. The theoretical density calculated from the determined lattice parameter and the bulk
density measured from the ratio of mass volume of all the studied samples. Table 2 shows the lattice parameter, bulk and theoretical density and porosity as a function of concentration of x for all the compositions. Fig. 4 (a) and Fig. 4 (b) shows the density and porosity as a function of x for all the composition respectively. The bulk density is lower than the X-ray density. This may be due to the existence of pores which were formed and developed during the sample preparation or the sintering process. The X-ray and bulk density increase with the increase of Sn content due to the higher atomic weight and density of Sn.

### 3.2 Frequency Dependence of Dielectric Constant

Fig. 5 shows the variation of dielectric constant with frequency from 1 kHz to 13 MHz at room temperature. The dielectric constant decreases with increasing frequency which is rapid at lower and slower at higher frequencies. This is a normal dielectric behavior observed in most of the

![Dielectric Constant vs Frequency Graph](image)

**Fig. 5.** Variation of dielectric constant with frequency for all the composition.

Ferromagnetic materials, which may be due to the interfacial polarization as predicted by Maxwell and Wagner (Wagner, 1913; Jadhav et al., 2008). High value of dielectric constant is in the order of $10^3$-$10^5$ at low frequencies. The inhomogeneous double layer dielectric structure formed due to the Maxwell-Wagner interfacial type of polarization for these high values of dielectric constant which follows the Koops Phenomenological theory (Koops, 1951). The dielectric behavior of ferrites may be explained on the basis of dielectric polarization process which is similar to that of the conduction mechanism that takes place mainly by the hopping of electrons. Electrical conduction in ferrites is mainly due to hopping of electron between ions of the same element existing in more than one valence state and distributed randomly over crystallographically equivalent lattice sites. A number of such ions formed during the sintering of ferrites. Fe $^{2+}$ ions concentration give rise to electron hopping between Fe ions in +2 and 3+ valence states. The magnitude of exchange depends on the concentration of Fe $^{2+}$/ Fe $^{3+}$ ion pairs present in B site. The dielectric constant decreases with increasing frequency and then reaches a constant value due to the fact that beyond a certain frequency of external AC field, the electron exchange between Fe $^{2+}$ and Fe $^{2+}$ cannot follow the
alternating field. This type of dielectric behavior was observed in a number of ferrites such as Cu-Cd ferrites, Li-Mg-Ti ferrites (Gurta et al., 2007), Mg-Cu-Zn ferrites (Basker et al., 2004), and Ni-Cu-Zn ferrites (Yue et al., 2003).

3.3 Resistivity

Resistivity is an important electrical property of ferrite materials. The electrical properties of ferrite materials depend upon the method of preparation, chemical composition, grain size and sintering temperature. The AC resistivity has been calculated using the formula:

\[ \rho = \frac{RA}{L} \]  \hspace{1cm} (1)

Where, R is the resistance, A is the cross-sectional area and L is the height of the samples. The temperature dependence of electrical resistivity of Ni\(_{0.6-x/2}\)Zn\(_{0.4-x/2}\)Sn\(_x\)Fe\(_2\)O\(_4\) ferrites of different compositions has been investigated. Fig. 6 shows the variation of AC resistivity as a function of temperature. The relationship between resistivity and temperature may be expressed by Arrhenius relation (Smit and Wijn, 1959) as,

\[ \rho = \rho_0 e^{\frac{E_a}{k_BT}} \]  \hspace{1cm} (2)

where, T is the absolute temperature, \(k_B\) the Boltzman constant and \(E_a\) is the activation energy. It is seen that the electrical resistivity decreases with 10\(^3\)/T for all the studied samples according to equation (2) exhibiting the semiconducting nature of the samples. From the Fig. 6 one can observe that in the investigated temperature range, the resistivity decreased by about three orders of magnitude. This strong increase in the conductivity with temperature must be regarded mainly as due to the thermally activated mobility of charge carriers, but not to a thermally activated creation of these carriers.

![Fig. 6. Temperature dependence resistivity for all the composition.](image)

Table 3 shows activation energy for all samples. It is observed that activation energy decreases with increasing Sn content. It is noted that the high activation energy goes hand in hand with low
conductivity of the ferrite. This is in good accordance with the conclusion that the lower activation energies are associated with higher electrical conductivity while higher activation energies are associated with lower electrical conductivity.

Table 3 Activation energy for various Ni_{0.6-x/2}Zn_{0.4-x/2}Sn_xF_2O_4 compositions.

<table>
<thead>
<tr>
<th>Sn content, x</th>
<th>Activation energy, E_a (MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>63</td>
</tr>
<tr>
<td>0.05</td>
<td>47</td>
</tr>
<tr>
<td>0.1</td>
<td>71</td>
</tr>
<tr>
<td>0.15</td>
<td>29</td>
</tr>
<tr>
<td>0.2</td>
<td>21</td>
</tr>
</tbody>
</table>

4. Conclusions

From the XRD patterns it can be concluded that the synthesized ferrite compositions are of single phase cubic spinel since no ambiguous reflections other than the spinel structures are evidenced. The increase in lattice parameter with increasing Sn content in these samples can be explained on the basis of the ionic radii. The temperature dependence of the dielectric constant and dielectric loss tangent increases while frequency dependence of the dielectric constant and dielectric loss tangent decreases for all the samples.

The resistivity changes monotonically with increasing Sn concentration in the system. The resistivity and dielectric constant are found to decrease with increasing frequency exhibiting normal ferromagnetic behavior of the samples. Dielectric constant increases as the temperature increases, which is the normal dielectric behavior of the magnetic semiconductor ferrite. The dielectric constant has abnormally high values and the dielectric loss exhibits a dielectric relaxation process or peaks at relatively higher temperatures. The activation energy decreases with increasing Sn concentration in the system. The lower activation energies are associated with higher electrical conductivity. The electrical conduction in these ferrites is explained on the basis of the hopping mechanism. The increase in frequency enhances the hopping frequency of charge carriers resulting in an increase in the conduction process thereby decreasing the resistivity. It is observe that in the investigated temperature range, the resistivity decreased with the increase temperature ensuring the semiconducting nature for all the samples of this spinel oxide. This strong increase in the conductivity with temperature must be regarded mainly as due to the thermally activated mobility of charge carriers, but not to a thermally activated creation of theses carriers.
References


