ELECTRIC AND SPECTROSCOPIC CHARACTERIZATION OF MIXED FERRITES OF NI-ZN-CU

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ABSTRACT

The NiZnCu ferrite system is prepared by the standard ceramic double sintering method. The single phase formation of it is confirmed through XRD. The value of dielectric constant, conductivity, activation energy and tanδ are measured. The conductivity values (at 150°C and at 10 kHz) ranges from $9.343 \times 10^{-5}$ S cm$^{-1}$ to $1.24 \times 10^{-3}$ S cm$^{-1}$ and dielectric constant varies from 112 to 405, the activation energy falls in between 0.266 and 0.347 and the tanδ varies from 1.491 to 5.55. Further confirmation of structural details of the ferrite is done with the help of FTIR spectrum.

KEY WORDS: Ferrites, dielectric constant, conductivity, activation energy, FTIR.

1. INTRODUCTION

Ferrites are candidate substances which find wide applications in microwave devices, computer memories and magnetic recording. They offer low eddy currents and dielectric losses for the propagation of electromagnetic waves within the range of frequencies up to few GHz. In view of their importance several researchers have studied (Elsa E Sileo, 2002; Vijaya kumar and Ravinder, 2002; Jacob, 2002) the electric and magnetic properties of ferrite materials in the past few years.

2. EXPERIMENTAL

Mixed ferrites of Ni$_{0.5-x}$Zn$_x$Cu$_{0.5}$Fe$_2$O$_4$ spinel system are prepared by standard ceramic double sintering method where $x = 0.0$ to 0.5. The samples are prepared by mixing the appropriate oxides namely NiO, ZnO, CuO and Fe$_2$O$_3$ in stoichiometric proportion and then pre-sintered at about 900°C for 20hrs and furnace cooled at the rate of 100°C per hour. The pre-sintered powders are palletized at the pressure of 70kg/cm$^2$ and then sintered at 1100°C for 20 hrs and furnace cooled at the rate of 100°C per hour. The pellets are taken out and the single phase formation of the sample is confirmed through XRD then they are subjected to different characterization using, Electric and Spectroscopic techniques.

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conductivity explains that the mixed ferrites have more electrons available for transport at higher frequencies. The variation of dielectric constant with frequency in these materials is explained to be due to the effective value of polarization caused by inter-ionic, molecular and grain boundary effects at low frequencies. The low values of dielectric constant at high frequencies are attributed to a less contribution of polarization due to exclusively interionic type.

Table-1 Conductivity, dielectric constant, tanδ, activation energy of sintered Ni0.5xZn1Cu0.5xFe2O4 system.

<table>
<thead>
<tr>
<th>Concentration x</th>
<th>Conductivity at 150°C σ at 10 kHz 10−4 Sm−1</th>
<th>At 150°C and 10 kHz frequency</th>
<th>Activation energy E0 eV at 10kHz Dielectric constant (ε')</th>
<th>tanδ</th>
<th>E0 eV at 10kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.24×10−4</td>
<td>405.186</td>
<td>5.55</td>
<td>0.2784</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>9.34×10−5</td>
<td>112.633</td>
<td>1.491</td>
<td>0.2867</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>2.80×10−4</td>
<td>184.479</td>
<td>2.732</td>
<td>0.3476</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>1.59×10−4</td>
<td>173.303</td>
<td>1.592</td>
<td>0.3325</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>1.46×10−4</td>
<td>122.635</td>
<td>2.149</td>
<td>0.3431</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>2.36×10−4</td>
<td>114.648</td>
<td>3.730</td>
<td>0.2660</td>
<td></td>
</tr>
</tbody>
</table>

The conduction mechanism for the samples of present study is due to hole transfer from Ni3+ to Ni2+ ions (Van Uitert, 1955). As zinc is a non-magnetic element and ZnFe2O4 is a normal ferrite, Zn2+ ions occupy tetrahedral A-site, while in NiFe2O4, a predominantly inverse ferrite, Ni2+ ions occupy octahedral B-site. In samples sintered at higher temperature, Ni3+ may also be present along with Ni2+ and hopping of holes from Ni2+ to Ni3+ is also probable according to the mechanism given above. So, in samples sintered at higher temperature, the conduction mechanism is enhanced and the conductivity of such samples is changed by an order of 102.

The curves of log(σ) versus 1000/T at 10 kHz for different concentration of Zn in the mixed ferrites are shown in the Fig.4. It is seen from the Fig.4 that conductivity is a direct exponential function of temperature, which is the inherent property of a semi-conductor. It is explained on the basis of hopping of electrons between localized 3d bands of ions in these mixed ferrites. The slope of the lines in the Figure-4 should be a measure of activation energy (E0). A hopping activation energy of the order of 0.1 eV is associated with the drift mobility of electrons (Ghani, 1984). However, if the observed values of activation energies are ≈ 0.2 eV suggest that the conduction mechanism observed is due to hopping of electron of the type Fe2+ ⇔ Fe3+. For ferrites possessing Cu and Ni in octahedral sites the value of activation energy has been reported to be ≈ 0.3797 eV (Rlinger and Samokhvalov, 1977). Thus there is a good agreement of the values of activation energy of the spinel system of the present study.

The measured values of activation energy versus concentration (Fig.5) would be able to throw more light on the changes in the position of the energy bands due to incorporation of Zn2+. This range of values is suggestive of hopping and the present system behaves like a semiconductor with intermittent energy levels in the localized d bands of neighboring Fe ions of B site. Based on these results we conclude that the Fe-3d electrons are important in the conduction process.
Conductivity measurement is indicative of the presence of Ni$^{2+}$ and Fe$^{3+}$ ions in B site. The rising up of activation energy ($E_{ac}$) with concentration is attributed to the widening of the band gap of 3d band of ions mainly in B site. The increase of concentration alters the composition of Ni and Zn. Generally Cu$^{2+}$ ion in B site is the cause of Jahn-Teller effect which makes the neighboring ions to go to the exited state.

### 3.2 FTIR analysis

The ferrites prepared in the present study crystallize in the natural spinel form with the space group Fd$_{3m}$ - (O$_h$). On the basis of group theoretical calculations, spinel ferrites exhibit four IR active fundamentals (T$_{ir}$) in the vibrational spectra of normal as well as inverse spinel ferrites. It has been reported that the first three IR bands are due to the tetrahedral (T$_d$) and octahedral (O$_h$) coordination compounds, while the fourth one is due to some type of lattice vibrations involving tetrahedral cation.

The infrared spectra of Ni$_{0.5-x}$Zn$_x$Cu$_{0.5}$Fe$_2$O$_4$, mixed ferrite samples are shown in the Figure-6 for different concentrations. The absorption bands obtained in the present investigation are found to be in the range reported for similar type of ferrites (Srinivasan, 1984; Waldron, 1955). The position of the bands together with their shoulders is given in the Table-2.

From Fig.6 it can be seen that the IR spectra of the present system exhibit five principal bands. The principal bands $v_1$ and $v_2$ shift gradually towards low frequency side mainly the high-frequency band ($v_1$) and second absorption band ($v_2$) are found to be in the range 660-670 and 580-560 cm$^{-1}$ respectively. A comparison of FTIR charts at different concentrations provides information about decrease in transmittance and increase in broadness.

![Figure 5: Variation of activation energy $E_{ac}$ with concentration ($x$) at 10kHz](image)

![Figure 6: FTIR spectra of the sintered Ni$_{0.5-x}$Zn$_x$Cu$_{0.5}$Fe$_2$O$_4$ system for different concentration.](image)

These features are explained on the basis of cation distribution in A and B sites of mixed Ni-Zn-Cu ferrites. Waldron (1955) has attributed the occurrence of $v_1$ and $v_2$ bands to the intrinsic vibrations of the tetrahedral (T$_d$) and octahedral (O$_h$) coordination compounds. Both these high frequency bands have been attributed to the intrinsic lattice vibrations of E-symmetry. The third absorption band $v_3$ is attributed to the Cu$^{2+}$ - O$^{2-}$ complexes at octahedral sites. The frequency of the ($v_4$ and $v_5$) bands depend on the mass of tetrahedral metal ion complexes (Josyulu and Sobhanadri, 1981) and hence it is attributed to the vibrations of ions at the tetrahedral site. The low frequency bands are attributed to vibrations of T$_{2g}$ - symmetry.

The proposed cation distribution of mixed Ni-Zn-Cu ferrites of the present study is:

\[
(Zn^{2+})_{x+y} (Fe^{3+})_{1-x-y} \cdot [Ni^{2+}]_{0.5-x} \cdot Zn^{2+} \cdot Cu_{0.5} \cdot Fe^{3+} \cdot (1+y) \cdot O^2-.
\]

Where $x = 0.1, 0.2, 0.3, 0.4$ and $0.5, y = 25\%$ of $x$.

As the content of Zn increases Zn$^{2+}$ ions consistently replace Fe$^{3+}$ ions from A to B site. At the same time Ni$^{2+}$ ions on the octahedral site decrease. This disturbs the order on the octahedral site with increase in zinc. The disordered systems give rise to broad bands in their spectrum (Patil, 1991).

Table-2 shows high frequency band in the range 670-660 cm$^{-1}$ which is found to decrease to a small extent with the increase of concentration. Consequently the changes in the high frequency band $v_1$ are correlatable to Zn$^{2+}$-O$^{2-}$ bond stretching. On the other hand second absorption band $v_2$ (580-560 cm$^{-1}$) which may be
attributed for Zn\(^{2+}\)-O\(^2\) at octahedral sites as it clearly indicates an appreciable decrease of frequency with increase of Zn concentration. The sites A and B are explained to possess other ions also in this mixed ferrites along with Zn. But the shifting of the band frequency is explained to be due to Zn ion concentration affecting the distribution of other ions. Based on these observations it is accounted for by that the expansion of B sites is larger than the expansion of A site. Third absorption band, explains John-Teller effect due to the presence of Cu\(^{2+}\) ion in octahedral sites. The presence of Cu\(^{2+}\) ions and the John-Teller splitting makes the companion’s ions of B site to exist in their exited states. It means that Ni\(^{3+}\) and Fe\(^{3+}\) ions in B sites may be shifted to Ni\(^{4+}\) and Fe\(^{4+}\) states. The explanation of this kind is in accordance with the inference of conductivity measurements. Consequently these results are in support of hopping of charge carriers from 3d bands of Ni and Fe ions. The variation of activation energy with concentration(x) has established that the band gap of localized 3d band widens. Widening of the band gap of 3d bands with x is co relatable to the relative strength of John-Teller splitting and crystal field in the octahedral site of spinel ferrite.

It is seen from the Table-2 that the frequencies of the bands \(v_1\) and \(v_2\) are found to be shifted from their corresponding values of end member ferrites namely NiFe\(_2\)O\(_4\), CuFe\(_2\)O\(_4\), ZnFe\(_2\)O\(_4\) and Fe\(_2\)O\(_4\). The larger difference of the frequency of \(v_2\) band found between end members and the present spinel ferrite may be attributed to the presence of many ion complexes and their masses in B site.

### Table-2 Center frequency of the bands of FTIR spectra of the sintered Ni\(_{0.5}\)Zn\(_{0.1}\)Cu\(_{0.5}\)Fe\(_2\)O\(_4\) system

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Center frequency cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X)</td>
<td>(v_1)</td>
</tr>
<tr>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>0.1</td>
<td>671.0</td>
</tr>
<tr>
<td>0.2</td>
<td>671.1</td>
</tr>
<tr>
<td>0.3</td>
<td>671.0</td>
</tr>
<tr>
<td>0.4</td>
<td>668.38</td>
</tr>
<tr>
<td>0.5</td>
<td>668.75</td>
</tr>
</tbody>
</table>

4. CONCLUSION

In the present investigation ferrite system is identified to understand the effect of encroachment of spin orbit interaction in the vicinity of crystal fields of Ni-Zn mixed ferrite by the substitution of Cu. The constituent ions of B site are subjected to excitation by initial impetus offered by spin orbit interaction of Cu\(^{2+}\) ions. In this ferrite the growth of Zn at the expense of Ni accentuates the widening of the gap of bands in the localized d bands.

REFERENCES


Jacob S E, Fano W G, Razzitte A C, The Effect of Rare Earth Substitution on the Magnetic Properties of Ni\(_{0.5}\)Zn\(_{0.1}\)M\(_{0.5}\)Fe\(_2\)O\(_4\) (M: rare earth), Physica B, 320 (1-4), 2002, 261-263.


