DC RESISTIVITY AND DIELECTRIC STUDIES ON Ti^{4+} SUBSTITUTED Ni-Zn FERRITES

B. Parvatheeswara Rao, K. H. Rao, T. Vasantha Rao, A. Paduraru[a], O. F. Caltun[a*]

Department of Physics, Andhra University, Visakhapatnam 530003, India
[a]Department of Electricity and Electronics, A. I. Cuza University, Iasi, Romania

$Ni_{0.65} Zn_{0.35+x} Fe_{1.99-2x} In_{0.01} Ti_x O_4$ with x values ranging from 0.000 to 0.125 in steps of 0.025 have been prepared by conventional ceramic technique. Studies were made to estimate the influence of the concentration of the Ti substitution on the dc resistivity and dielectric constant of these ferrites. The resistivity has been found to increase by increasing concentration of titanium ions. Resistivity versus temperature measurements were carried out in order to deduce the activation energies in both ferrimagnetic and paramagnetic regions. Temperature variation of resistivity was marked by an exponential fall with rising temperature up to Curie temperature. Increasing up the temperature further changes conduction mechanism and the resistivity increases. Activation energies corresponding to the slopes for both regions of each sample have been estimated. These values indicate that the titanium substitution blocks the dominant conduction mechanism. The dielectric constant has been found to exhibit a trend different from that of dc resistivity. The Ti ions induce lower dielectric constants in the doped systems. Dielectric dispersion exhibits normal behavior up to 2 MHz. The results are explained taking into account the conduction and polarization processes associated with the ions having different valence states and being distributed in different lattice sites.

1. Introduction

High valent additions/substitutions are often reported to be effective in controlling the losses and in improving the electrical and magnetic properties [1-4]. These characteristics are especially important if the investigations are to be carried out towards materials for power applications. The latest technological developments demand operating frequencies for ferrites beyond 1 MHz. Ni-Zn ferrites find an edge because of their better electrical and magnetic responses at higher frequencies. Thus, we have aimed at studying such materials with careful compositional modifications in order to get improvements, both in electrical and magnetic fronts. Polycrystalline nickel-zinc ferrite system with the chemical formula $Ni_{0.65}Zn_{0.35+x} Fe_{1.99-2x} In_{0.01} Ti_x O_4$ has been chosen for the present study. To minimize the magnetocrystalline anisotropy and to increase the resistivity a small quantity of indium replacing the iron ions was used [5]. By considering their specific site preferences zinc and titanium ions are preferred for simultaneous substitution to improve the basic properties of Ni-Zn ferrite [6,7]. However, the present paper reports and discusses the variations of dc resistivity versus composition and temperature. The dielectric constant and dielectric loss tangent dependence on doping level and frequency is described in detail.

2. Experimental details

$Ni_{0.65} Zn_{0.35+x} Fe_{1.99-2x} In_{0.01} Ti_x O_4$ samples with x values ranging from 0.000 to 0.125 in steps of 0.025 have been prepared by conventional ceramic technique. Sintering of the samples was

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* Corresponding author: caltun@uaic.ro

carried out in air atmosphere at 1250 °C for 4 hours followed by natural cooling. X-ray pattern of the composition $Ni_{0.65} Zn_{0.35} Fe_2 O_4$ confirms single phase cubic spinel structure. The Curie temperature and saturation magnetization values, comparable with values for ferrite having similar composition, were reported earlier [8]. Resistivity measurements were carried out using standard two probe technique and the dielectric measurements were made using HP 4192A Impedance Analyzer.

3. Results and discussion

Room temperature dc resistivity as a function of titanium doping level is shown in Fig. 1. The resistivity has been observed to increase continuously in whole range of titanium concentrations. Temperature variation of dc resistivity has been studied starting from room temperature to the temperature higher than Curie temperature. From plots of log (ρ/ρ_0) versus 1000/T activation energies were calculated for ferrimagnetic and paramagnetic regions. The plot for sample with $x=0.075$ TiO_2 is shown in Fig. 2. Rising the temperature before Curie temperature, as expected in ferrimagnetic region, the resistivity of the samples has been observed to fall exponentially. Beyond the Curie temperature the resistivity increases. The conduction mechanism changes causing phase transformation induced at temperatures higher than Curie temperature. Activation energy values corresponding to the slopes for each region and for all the samples have been estimated. The higher activation energy values have been found to correspond to samples exhibiting higher resistivities. The activation energy values lie in the range 0.13 – 0.26 eV.
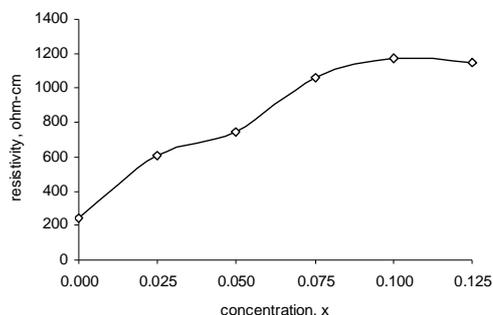

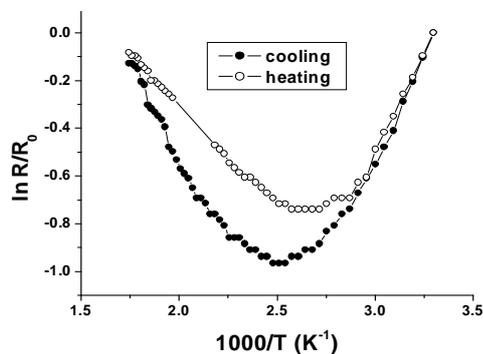Fig. 1. Variation of resistivity with Ti^{4+} concentration, x for the system $Ni_{0.65} Zn_{0.35+x} Fe_{1.99-2x} In_{0.01} Ti_x O_4$

Fig. 2. Variation of log of resistivity with temperature (1000/T) for the system $Ni_{0.65} Zn_{0.35+x} Fe_{1.99-2x} In_{0.01} Ti_x O_4$.

The influence of titanium concentration on the dielectric constant values, at 10 kHz, is shown in Fig. 3. Dielectric constants of these ferrites have been found to be of the order of 10^3. All the substituted samples have low dielectric constants than the basic composition (without titanium). However, increasing the substituents' concentration, starting with $x=0.025$, the dielectric constant increases slightly. The variation of dielectric loss tangent with titanium concentration is shown in Fig. 4. All the samples containing titanium exhibited lower dielectric losses compared to the basic composition. Figs. 5 and 6 show frequency responses of dielectric constant and dielectric loss tangent, tan δ, respectively for different titanium concentrations. The curves of dielectric constant versus frequency exhibit normal behaviors up to 2 MHz and then decrease rapidly. Some samples with lesser titanium concentrations or without titanium show dielectric peaks. Where as the losses, described by the curves tan δ versus frequency feature peaks in the MHz region for all the samples.

Since conduction takes place through hopping of electrons between ions of different valence states within the crystallographic positions without causing a change in the energy state of the crystal as a result of the transitions [9], the observed variation in resistivity with the substituents' concentration can be explained on the basis of occupation of cations in different lattice sites and hopping between them. For every substitution of zinc, it forces an equal number of Fe^{3+} ions to migrate to B-sites only to be replaced there by the titanium ions. This process of simultaneous

substitution of zinc and titanium does not affect the conduction as long as the total quantity of iron available in B-sites and thereby the Fe^{2+} ions remain the same. But, in order to maintain the charge balance, the quantity of iron replaced with every step of substitution is kept equal to both the quantities of titanium and zinc together. Thus, even though half of the iron replaced in B-sites is compensated by migration of equal quantity of the same because of zinc substitution, te other half equal to 0.025 Fe^{3+} ions effectively decrease in number in B-sites with successive step of substitution. This process consequently decreases the number of Fe^{2+} ions present for hopping and contributes to increase the resistivity. Further, the ability of Ti^{4+} ions to form locking pairs of Ti^{4+} - Fe^{2+} also contribute to enhance the resistivity. The resistivity modifications with titanium concentration are in agreement with the above.
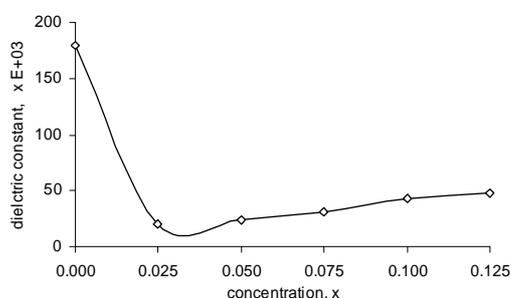

Fig. 3. The influence of Ti^{4+} concentration, x on dielectric constant at 10 kHz for the system $Ni_{0.65} Zn_{0.35+x} Fe_{1.99-2x} In_{0.01} Ti_x O_4$
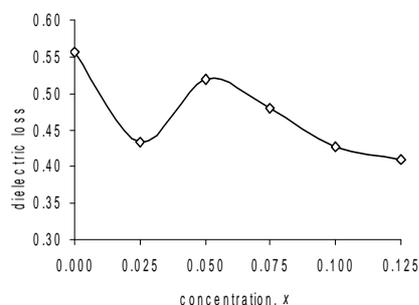

Fig. 4. The influence of Ti^{4+} concentration, x on dielectric loss tangent at 1 MHz for the system $Ni_{0.65} Zn_{0.35+x} Fe_{1.99-2x} In_{0.01} Ti_x O_4$.
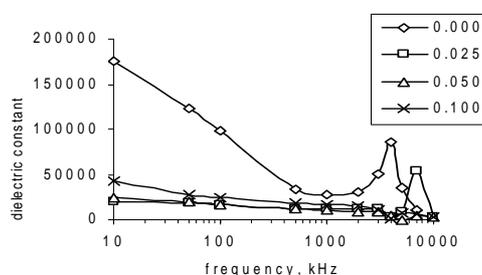

Fig. 5. Dielectric dispersion curves for sample for different titanium concentrations in the system $Ni_{0.65} Zn_{0.35+x} Fe_{1.99-2x} In_{0.01} Ti_x O_4$.
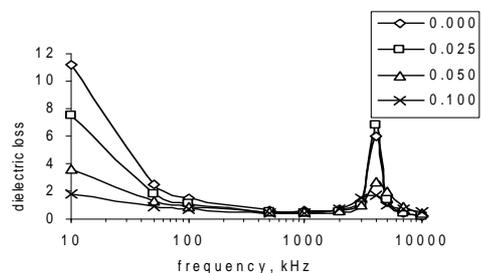

Fig. 6. Dielectric loss tangent, tan δ versus frequency for different titanium concentrations in the system $Ni_{0.65} Zn_{0.35+x} Fe_{1.99-2x} In_{0.01} Ti_x O_4$.

The log R/R_o versus 1000/T plots of all the samples exhibit typical semiconductor behavior and also a phase transformation beyond the Curie temperature. In the paramagnetic region, the conduction mechanism changes. The values for activation energy in ferromagnetic region (0.13 - 0.26 eV) suggest that the dominant conduction mechanism, such as $Fe^{2+} \Leftrightarrow Fe^{3+}$ for which the activation energies lie around 0.1 eV [10], does not enhance with the substituents' concentration and thus in support of the arguments made above.

The observed decrease in dielectric constant for substituted samples indicates that these cations help to slow down the conduction process between iron ions. The presence of Fe^{2+} ions in ferrites is known to produce large dielectric constants. On the other hand if titanium ions in B-sites block the hopping between charge carriers, the dielectric constants would slightly decrease. This is in agreement with the observed values of dielectric constants throughout the series. However, the slight increase in dielectric constant with increase in substituents' concentration may be due to corresponding changes in microstructures brought about by the sintering conditions.

Normal dielectric behavior up to 2 MHz can be explained on the basis of space charge polarization due to inhomogeneous dielectric structure [11]. The sudden decrease in dielectric

constant at 2 MHz and a peak in dielectric loss at the same frequency can be interpreted in terms of the dimensional effects in Mn-Zn ferrites [12].

4. Conclusions

Resistivity and dielectric measurements on Ni-Zn ferrites support the site occupancy of substituted cations of zinc and titanium in tetrahedral and octahedral sites respectively and these results, apart from activation energies, indicate that the hopping processes between the iron ions having different valence states is the dominant conduction mechanism. Frequency responses of dielectric constant and dielectric loss tangent reveal that these materials exhibit normal behavior up to 2 MHz and beyond which they experience resonances due to dimensions. Mössbauer spectroscopy and SEM studies on these samples are being planned and the information obtained from such studies would provide a clear picture about the contributions of substituted cations to the modification of the electrical and magnetic properties of the ferrites.

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