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INFLUENCE OF V_2O_5 ADDITIONS ON THE RESISTIVITY AND DIELECTRIC PROPERTIES OF NICKEL-ZINC FERRITES

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Ni-Zn ferrites with the formulae $Ni_{0.65}Zn_{0.35}Fe_2O_4 + xV_2O_5$ where x values ranging from 0.0 wt% to 1.5 wt% in steps of 0.3 wt% have been prepared by conventional ceramic technique. Single phase cubic spinel structures were confirmed by X-ray diffraction patterns. For increasing addition of vanadium up to 0.6 wt% the resistivity of the system has been found to increase. High addition concentration, up to 1.2 wt%, are followed by slow decrease of the resistivity. The variation of the resistivity versus temperature was studied and the activation energies corresponding to the ferrimagnetic and paramagnetic regions for each sample have been estimated. The dielectric constant of the system has a variation quite opposite to that of dc resistivity. A slow variation of the dielectric loss tangent with the additive concentration has been found for all the samples. The sample without addition show lower values of the loss tangent. The results are explained in terms of the conduction and polarization processes associated with the distribution in the lattice of the ions having different valences.

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1. Introduction

Soft magnetic ferrites with pentavalent additions are interesting materials for high frequency power applications [1,2]. The effect of V_2O_5 and Nb_2O_5 additions on the microstructure and power losses of Mn-Zn ferrite was recently studied [3]. It was observed that the sintered density of the materials increases monotonously with total amount of the dopants and the sintering temperature. The grain size remains small for all the samples sintered in soft temperature condition. Pentavalent niobium and tantalum additions have been tried and found useful with Mn-Zn and Ni-Zn ferrite systems [4,5]. However, the impact of pentavalent vanadium ions is still to be established in these ferrite systems. Therefore, an attempt has been made to understand the influence of vanadium ions on various electrical and magnetic properties of Ni-Zn ferrites. This paper presents the result of the experiment done on the dc resistivity variation versus the additive concentration and temperature. The dependence of the dielectric constant and of the dielectric losses on composition and frequency were studied.

2. Experimental details

$Ni_{0.65}Zn_{0.35}Fe_2O_4 + x\,V_2O_5$ with x values varying from 0.0 to 1.5 wt% in steps of 0.3 wt% have been prepared by conventional ceramic technique. Sintering of the samples was carried out in air atmosphere at 1210 °C for 4 hours followed by natural cooling. X-ray patterns of the samples confirm single phase cubic spinel structures. Characterization of the samples was further done by measuring lattice constant, Curie temperature and saturation magnetization. The values are in the same range as the values of the respective parameters for same composition reported earlier [7].

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Resistivity measurements have been made by standard two probe method and the dielectric measurements are made using HP 4192A Impedance Analyzer.

3. Results and discussion

Variation of dc resistivity as a function of vanadium concentration is shown in Fig. 1. Increasing the additive concentration, up to 0.6 wt%, the resistivity increases. Higher concentration of the vanadium ions, up to 1.2 wt%, entails lower values of the dc resistivity. Stepping up the concentrations, up to 1.5 wt%, the dc resistivity increases. Temperature variation of dc resistivity has been studied starting from room temperature to the temperature higher than Curie temperature. From the plots of log (ρ/ρ_0) versus 1000/T, activation energies were calculated for ferimagnetic and paramagnetic regions. The plot for sample with 0.6 wt% V_2O_5 is shown in Fig. 2. As expected for semiconductors, the resistivity of the samples has been observed to fall exponentially with rising temperature before Curie temperature. After this, the conduction mechanism changes and the resistivity increases. Activation energy values corresponding to the slopes for each sample in both the regions have been estimated and are resumed in Table 1. Higher activation energy values have been found to correspond to samples exhibiting higher resistivities.

Table 1. The activation energy for increasing concentrations of V_2O_5 addition. ΔW_1 the activation energy in ferrimagnetic region, ΔW_2 the activation energy in paramagnetic region.

Sample	Concentration of V_2O_5(wt%)	ΔW_1(meV)	ΔW_2(meV)
V1	0	136.6	77.33
V2	0.3	52.79	75.21
V3	0.6	205.49	61.82
V4	0.9	134.58	39.65
V5	1.2	150.66	40.03
V6	1.5	101.54	78.29

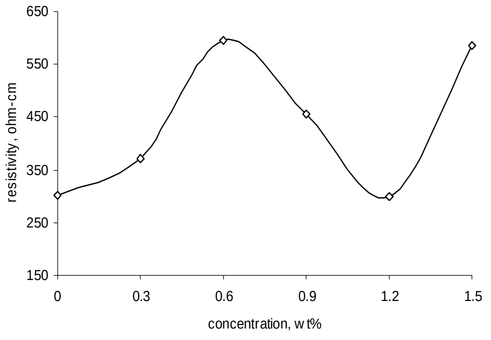

Fig. 1. Variation of resistivity with vanadium concentration for $Ni_{0.65}Zn_{0.35}Fe_2O_4 + x V_2O_5$ system.

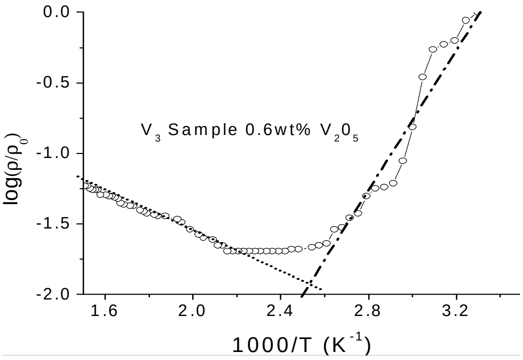

Fig. 2. Log (ρ/ρ_o) versus 1000/T for $Ni_{0.65}Zn_{0.35}Fe_2O_4 + x V_2O_5$ system.

Variation of dielectric constant, (ε') determined at 10 kHz, as a function of vanadium concentration is shown in Fig. 3. The ε' has been found to exhibit a trend opposite to that of dc resistivity. Fig. 4 shows the variation of tan δ with vanadium concentration. The tan δ is observed to be higher for vanadium doped samples. Variations of dielectric constant and dielectric loss tangent with frequency for the sample with 0.3 wt% V_2O_5 doping level are shown in Figs. 5 and 6. The dielectric constant and the tan δ are found to exhibit normal dielectric behavior up to lower megahertz region while showing peaks around 4 MHz.

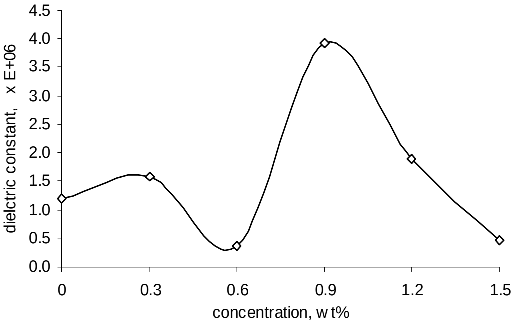

Fig. 3. Variation of dielectric constant with vanadium concentration at 10 kHz for $Ni_{0.65}Zn_{0.35}Fe_2O_4 + x\,V_2O_5$ system.

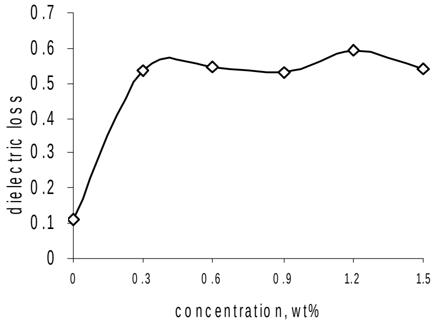

Fig. 4. Variation of dielectric loss tangent with vanadium concentration at 10 kHz for $Ni_{0.65}Zn_{0.35}Fe_2O_4 + x\,V_2O_5$ system.

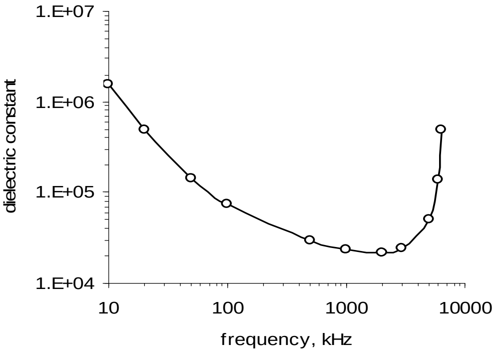

Fig. 5. Typical dielectric constant for the addition of 0.3 wt% V_2O_5 in $Ni_{0.65}Zn_{0.35}Fe_2O_4$.

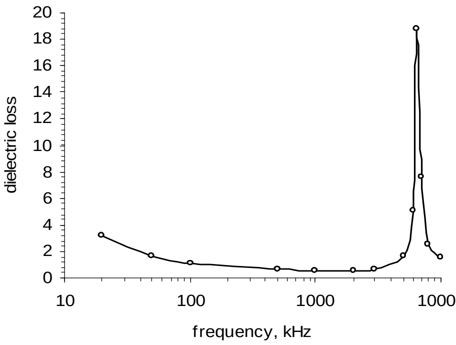

Fig. 6. Typical variation of tan δ with frequency for the addition of 0.3 wt% V_2O_5 in $Ni_{0.65}Zn_{0.35}Fe_2O_4$.

Verwey and de Boer [8] established that an electronic exchange such as $Fe^{2+} \Leftrightarrow Fe^{3+}$ takes place in the crystallographically equivalent sites without causing a change in the energy state of the crystal as a result of the transitions. Van Uitert [9] confirmed the production of such ions in more than one valence state during the preparation of ferrites due to volatilization of zinc. Hopping between A-A sites does not exist for the simple reason that any Fe^{2+} ions formed during processing preferentially occupy B-sites only. Thus, the variations in resistivity may be explained either by hopping probabilities of the cations present in B-sites or by the microstructural modifications brought about by the sintering conditions or the both. The observed variation of resistivity with vanadium concentration in the present system may be explained in terms of the dissolution of the vanadium in the lattice and corresponding production and occupation of Fe^{2+} ions apart from V^{5+} ions in B-sites and also due to segregation of vanadium at grain boundaries at higher concentrations.

From the plots of log (ρ) versus 1000/T, the conduction processes contributing to the modification the resistivity can be understood as follows: if the conduction process is due to diffusion process of electrons of the type $Fe^{2+} \Leftrightarrow Fe^{3+}$, the associated activation energies would be of the order of 0.1 eV [9]. If the migration is expected via Ni^{2+} or Fe^{3+} neighbors i.e., the exchange process is of the type $Ni^{3+} + Fe^{2+} \Leftrightarrow Fe^{3+} + Ni^{2+}$ then the associated activation energies for this process would be higher of the order of 0.3 eV [11]. But the observed values of activation energy lie in between and suggest that the conduction processes may be governed by the dominant mechanism of diffusion process and some more mechanisms, involving the vanadium ions, play an important role in determining the properties.

The dielectric behavior in ferrites can be explained on the basis of the assumption that the mechanism of dielectric polarization is similar to that of conduction. There have been reports of strong correlation between the conduction mechanism and dielectric constant of ferrites [12,13]. In these works, the dielectric behavior is explained on the basis of number of available Fe^{2+} ions in the octahedral sites. The electronic exchange such as $Fe^{2+} \Leftrightarrow Fe^{3+}$ results in a local displacement of electrons, which determines the polarization and thus the dielectric constant of ferrites. The addition of pentavalent vanadium ions is expected to enter the lattice initially, modify the microstructure and also the available charge carriers for polarization. It is reported that pentavalent additions, by entering into lattice, modify the valence states of iron, producing more Fe^{2+} ions in order to maintain the charge balance [6]. The observed higher values of dielectric constants for the vanadium added samples are in accordance with this explanation. However, subsequent additions seem to prevent the development of the microstructures, thus contributing to the of decrease the dielectric constants with the increase in vanadium concentration.

The dielectric dispersion can be explained on the basis of Koop's two layer model and Maxwell-Wagner polarization theory. To interpret the frequency response of dielectric constant in ferrite materials, Koops [14] suggested a theory in which relatively good conducting grains and insulating grain boundary layers of ferrite material can be understood as given by an inhomogeneous dielectric structure, as discussed by Maxwell [15] and Wagner [16]. Since an assembly of space charge carriers in the inhomogeneous dielectric structure requires finite time to line up their axes parallel to an alternating electric field, the dielectric constant naturally decreases, if the frequency of the field reversal increases. This is in agreement with the observed dielectric dispersion up to 2 MHz. The observed peaks in the dielectric constant and dielectric loss tangent at around 4 MHz are considered to be the results of dimensional resonance and the same may be verified after evaluating the permeability of these samples.

4. Conclusions

The results indicate that the pentavalent vanadium additions in Ni-Zn ferrites lead to opposite trends for resistivity and dielectric constants. The frequency response is normal up to a few MHz followed by flux reversal accompanying dielectric peaks around 6 MHz. Microstructural and structural modifications due to the vanadium additions are considered to explain the results. Chemical analyses to estimate the Fe^{2+} concentration and micrographs to understand the grain and grain boundary structures on these samples would consolidate the conclusions further.

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