Improved electromagnetic properties of Vanadium doped Ni-Zn ferrite for high frequency Applications

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Abstract- A series of samples with the composition Ni₀.₆₅ Zn₀.₃₅ Fe₂ O₄ + x V₂ O₅ (x = 0.0 to 1.5 wt % in steps of 0.3 wt %) have been prepared by double sintered ceramic method. They are calcined for four hours at 900°C and sintering temperature is maintained at 1210°C at for 4 hours in air atmosphere. The samples are characterized by X-ray diffraction, Saturation magnetization and Curie temperature. Both the saturation magnetization and Curie temperature have been observed to decrease slightly with increasing concentration of the vanadium. An increasing trend in D.C. resistivity is observed in vanadium series up to x = 0.6 wt%. The μ_i is decreased slightly for lower concentrations and steeply for higher concentration. Higher resistivity and near stable magnetic properties are exhibited with vanadium concentration x = 0.6 wt%. Dissolution of Vanadium into ferrite lattice for minor additions is responsible for the modifications in the electrical and magnetic properties.

Keywords: Curie temperature, d.c resistivity, ferrites, saturation magnetization

I. INTRODUCTION

Ni-Zn ferrites are very attractive from the commercial point of view for the use of large number of applications in a wide frequency range. Several investigators [1, 2] have studied the electrical and magnetic properties of Ni-Zn ferrites with different additives. Improved electrical properties and degraded magnetic properties have been reported by the addition of tetravalent ions. Addition of trivalent ions enhanced the magnetic properties slightly. Additions of divalent ions decreased electrical conductivity. However, minor addition of pentavalent ions influence on the properties of Ni-Zn ferrites seems to have received very little attention.

II. PAST EXPERIMENTAL WORK

Homogeneous microstructure and higher permeability is reported by JunHu et al [3] in the same composition x in steps of 0.3 wt%. Vanadium substitution in place of Fe brought in grain growth and decreased Curie temperature is reported by M.Kaiser et al [4]. O.Mirzaee et al observed improvement in electromagnetic properties. The related research work suggested vanadium addition in nickel zinc ferrite could have a positive influence on the desired properties. It is desirable to bring out a systematic study of Ni-Zn ferrites substituted with pentavalent ions not only to estimate their influence on the electromagnetic properties on one hand but also to understand the methods of such changes on the other. It is proposed to investigate the effect of V₂O₅ addition in Ni-Zn ferrites in this work.

III. EXPERIMENTAL DETAILS

Analytical reagent grade oxides, on the basis of purity and particle size, are used for preparation of the Ni₀.₆₅ Zn₀.₃₅ Fe₂ O₄ + x V₂ O₅ ferrite samples. The samples are prepared by a double sintered ceramic method. They are pre-sintered for four hours at 900°C and sintered in air atmosphere at 1210°C for 4 hours. X-ray diffraction studies were done using Philips X-ray diffractometer. Entire samples exhibit single phase spinel structure. Curie temperature was measured by the simple technique described by Sooho. The error in this measurement was about ±5 oC. Saturation magnetization
measurements were obtained by the pendulum (Ponderometer) method, given by Rathnov. Initial permeability values are obtained from inductance measurements. DC resistivity values have been obtained by a two-probe method.

IV. RESULTS AND DISCUSSION

A. Magnetic Properties

Curie temperature
It has been observed to decrease slightly with the vanadium ion concentration. The decrease being almost linear, $5^\circ C$ for every increasing step, as shown in figure 1. These variations are explained with the help of exchange interactions.

![Fig. 1. Variation of Curie temperature with vanadium concentration (x) in Ni$_{0.65}$Zn$_{0.35}$Fe$_2$O$_4$ + x V$_2$O$_5$](image)

According to Neel’s molecular field theory, there exists three types of exchange interactions in ferrites (A-A, B-B, and A-B interactions); and the AB interaction predominates over the other. The exchange interaction depends on the ions density and magnetic moment.

If the doped V$^{5+}$ ions enter the spinel lattice, they may prefer to occupy B-sites which decrease the density of magnetic ions present at those sites and a decrease of this sub-lattice magnetic moment is also expected. This weakens the A-B exchange interactions and explains the Curie temperature decrease. If the minor addition of V$^{5+}$ ions prefer the A-sites it could lead to migration of some ferric ions from A-sites to B-sites and this must be accompanied by an increase in magnetization. It is also proposed that this migration would result in ferrous ions in octahedral site and this decreases the magnetization [5, 6]. This can be understood with the explanation that vanadium ions, while entering the lattice, may modify the existing cations valence states such as Fe. If the ferric ions with 5 $\mu$B are modified into ferrous ions with 4 $\mu$B of magnetic moment, they result in weakening the A-B exchange interactions marginally and thus explain the slight decrease in Curie temperature.

Saturation Magnetization
The variations in saturation magnetization (Ms) versus vanadium concentration are shown in Fig.2. Near stable saturation magnetization values are observed up to x = 0.6 wt % decreased for higher wt% concentrations. The introduction of vanadium ions with certain preference for B sites into a composition of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ [6, 7] is expected to dilute the B-sub lattice and the net magnetization should decrease with the increase in vanadium concentration.

![Fig. 2. Variation of saturation magnetization (M) and initial permeability ($\mu_i$) at 10 kHz (b) with vanadium concentration (x) in Ni$_{0.65}$Zn$_{0.35}$Fe$_2$O$_4$ + x V$_2$O$_5$](image)

But, as the vanadium is not replacing any ions of the host system, the total number of magnetic ions in the system, irrespective of the vanadium content, remains same. Therefore, the resultant value of Ms is decreased rather slowly or maintains almost a constant for lower wt% concentrations.

A different explanation may be offered for the decrease of saturation magnetization of subsequent concentration. This may be due to modification of some of the trivalent iron ions into divalent iron ions. Locking pairs of these divalent iron ions with vanadium ions may increase the distance between bonding ions and decrease the exchange interactions strength further. However, confirmation of such divalent iron ions, vanadium ions site occupancies and their dissolution limits in the lattice can be done only by conducting further studies on these samples.

Initial permeability
Observed variations of initial permeability ($\mu_i$) with vanadium concentration at 10 kHz at room temperature are given in figure 2 (b). $\mu_i$ is observed to decrease slightly with
vanadium content for 0.3 wt% concentration. Thereafter, the value of $\mu_i$ is increased and remains same up to 0.9 wt% concentration and then decreased for subsequent increase in vanadium concentration [8]. The trends of initial permeability variations are similar to the saturation magnetization variations with wt% concentration. Since, permeability depends on saturation magnetization the variations of permeability can be understood as a follow up of saturation magnetization

$$\frac{\text{D.C. Resistivity}}{\text{Activation energy}}$$

Hopping mechanism explains the conduction of ferrites. If the conduction is due to electrons diffusion, i.e. $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$, the associated activation energies would be 0.1 ev [10]. If the migration of electrons is expected from $\text{Ni}^{2+}$ or $\text{Fe}^{3+}$ neighbors i.e., the exchange process would be $\text{Ni}^{3+} + \text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} + \text{Ni}^{2+}$. Then the activation energy must be higher than 0.3 eV [11]. But the observed values of activation energy shown in figure 3, lie in the range of 0.2-0.3 ev and this suggested that the conduction in these ferrites may be due to dominant mechanism of diffusion process and some more mechanisms, involving the vanadium ions.

V. CONCLUSIONS

Moderate saturation magnetization has been observed throughout the dopant concentration and Curie temperature was found to be reasonably high, i.e. 370°C. Initial permeability and saturation magnetization values have been observed as 340 and 78.5 emu/g respectively at 0.6 wt% of vanadium addition. Improved electromagnetic properties are observed for $x = 0.6$ wt% vanadium concentration. These materials are found suitable for high frequency applications. The variations are explained on basis of dissolution of vanadium into the Ni-Zn ferrite lattice at lower concentrations and grain boundaries at higher concentrations.

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