Magnetic and Electrical properties of $Ni_{0.65-x}Co_xZn_{0.35}Fe_2O_4$

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Abstract*-A series of samples with composition Ni0.65-xCoxZn0.35Fe2O4 has been prepared by conventional ceramic method. The effect of anisotropic contribution of cobalt on saturation magnetization and initial permeability has been discussed with a view to extend frequency of operation. The variations of magnetic and electrical properties have been explained in the light of modified cationic environment. The improvements in saturation magnetization and D.C. resistivity offered the possibility in shifting the critical frequency of operation.*

I. INTRODUCTION

The extensive study of several researchers on mixed ferrite systems has revealed that Ni-Zn ferrite (Ni0.65Zn0.35Fe2O4) was the only core material useful for high frequency applications up to 100 MHz due to its high value of magnetization, high permeability, low power loss, low dielectric loss, high Curie temperature and high resistivity. The critical frequency of operation of a magnetic core is proportional to square of saturation magnetization and dc resistivity, inversely proportional to grain size and initial permeability as [1]

$$f_c \ \alpha \ M_s^2 / \mu_i \ . \ Df_c \ \alpha \ \rho / D^2$$

The maximum values of saturation magnetization and dc resistivity for the bulk Ni-Zn ferrite are reported [2] to be 73 emu/g and 106Ω-cm, respectively. In order to shift the frequency of operation of these core materials for microwave applications, there is a need to develop the Ni-Zn ferrite system with the highest magnetization possible coupled with sufficiently high electrical resistivity. Selection of proper impurity, optimization of processing conditions and control on grain size are the necessary parameters to obtain the desired electromagnetic properties of ferrites. Improvements in electrical resistivity and saturation magnetization have been reported by substituting small amounts of cobalt replacing nickel [3] in Ni0.50Zn0.50Fe2O4. Since initial permeability is related to saturation magnetization (µi α Ms2) significant enhancement in permeability may be expected with the substitution of cobalt in place of nickel[R]. A reduction in initial permeability can be anticipated by substituting cobalt due to its large contribution to anisotropy at octahedral site [4]. Rezlescu et. al. [5] studied the electric and magnetic properties of Ni-Zn ferrites up to 12.5 mol % till which cobalt ions have their preferential occupancy towards octahedral sites. This paper describes the magnetic and electrical properties of a familiar composition Ni0.65Zn0.35Fe2O4 by incorporating cobalt till 12.5 mol % replacing nickel ions.

II. EXPERIMENTAL DETAILS

Samples having the general composition Ni0.65-xCoxZn0.35Fe2O4 (x = 0.00 to 12.5mol % in steps of 2.5mol %) were processed through conventional ceramic method. In the process, annealing temperatures are 950oC for 4 h whereas sintering temperatures are 1250o C for 2 h in air atmosphere. Single phase spinel structure was observed for all the series of samples. X-ray diffraction patterns of all the samples were recorded using Cu-Kα radiation. Saturation magnetization for all the samples was measured using Ponderometer method [6]. Curie temperature was determined using Soohoo method [7]. Inductance values were measured using HP4192A LF Impedance analyzer at the small voltage of 1mV at a frequency of 1 kHz. DC resistivity was estimated using two-probe method. Determination of Hall voltages was carried out using the traditional vanderPauw technique [8] by applying a uniform low magnetic field of induction 1000 G exactly along the thickness at right angles. Estimation of grain size for each composition was performed on optical microscope. Anisotropy constants were calculated using initial permeability, saturation magnetization and grain size [9].

III. RESULTS & DISCUSSION

The study of magnetic and electrical properties of a selected composition is essential to understand the mechanism of achieving the higher critical frequency of operation for these materials, which is critical for microwave applications. The lattice constant of the basic Ni-Zn ferrite (8.3830 Å) is in agreement with that of the reported [10]. Gradual increase in lattice constant is observed with increasing cobalt concentration (Table1). Increase in lattice constant is attributed to larger ionic radius of Co2+ ion (0.745 Å) [11] compared to Ni2+ ions (0.69 Å) which suggests the entry of cobalt into the spinel lattice throughout the series.

Magnetic properties

Specific saturation magnetization and Curie temperature

The specific saturation magnetization is observed to increase linearly with the cobalt concentration, reaching a maximum value 82.1 emu/g (Fig.1). The observed increase in magnetization can be understood on the basis of Neel model in which A-B exchange interaction in ferrites is stronger and effective than A-A and B-B superexchange interactions and the net magnetic moment of the ferrite lattice as a whole is equal to the difference between the magnetic moments of A and B sublattices, i.e. M = MB-MA. As Co2+ ions are known to have their preference for octahedral site [5], can readily replace Ni2+ ions which have usual tendency to occupy octahedral sites in bulk Ni-Zn ferrites. The magnetic moments of divalent cobalt and nickel are 3μB and 2μB respectively and inclusion of cobalt ion at B-site increases the magnetic moment of the B-sublattice while the magnetic moment of A-site remains unaffected. Thus increasing cobalt concentration, the total magnetic moment of the spinel lattice and hence the net specific saturation magnetization increases. Incorporation of cobalt ions at B-sites strengthens A-B and B-B interactions in the ferrite lattice. Therefore a greater amount of thermal energy is needed to offset the effect of exchange interactions and the same is depicted through Curie temperature measurements (Table1).

Table1. Variations of lattice constant (a), specific saturation magnetization(σ), Curie temperature (Tc), initial permeability (μi), resistivity (ρ), Hall voltage(VH), first order anisotropy constant (K1) with cobalt concentration (x mole%)

X (mole %)	a (^{0}A)	σ(emu/g)	T_c (^{0}c)	μ_i	ρ×10^4 (Ωcm)	V_H (volts)	K_1×10^4 (erg/cm^3)
0	8.383	74.5	387	421	4.42	0.236	3.67
2.5	8.392	76.23	394	380.4	14.11	0.27	3.65
5	8.397	77.6	402	207	22.3	0.328	5.71
7.5	8.4023	79.1	411	172.6	48.7	0.357	6.73
10	8.4052	80.6	419	142.8	74.65	0.38	8.86
12.5	8.409	82.1	428	102.4	103.4	0.445	11.11

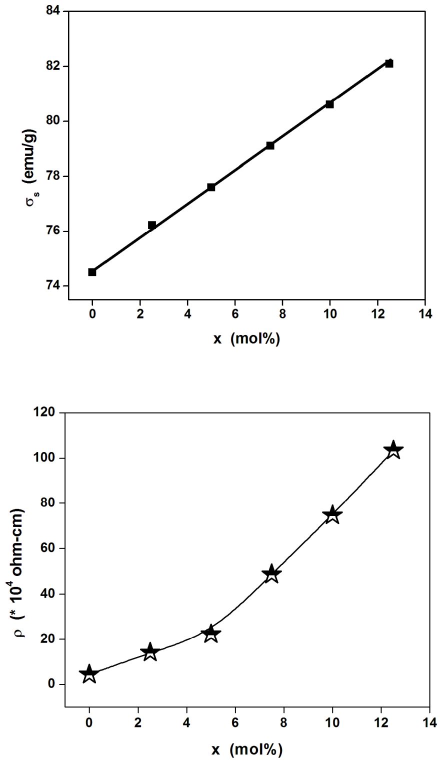

Fig. 2 variations of a) specific saturation magnetization b) dc resistivity with cobalt concentration(x)

Initial permeability

A decrease in initial permeability is noticed throughout the cobalt concentration studied as shown in figure. The value of initial permeability for the basic Ni-Zn composition found to be 430 which is in close agreement with that of the reported [12]. In general, initial permeability increases with increase in saturation magnetization since materials with high magnetization facilitate flow of maximum electromagnetic flux. The decrease in initial permeability can be attributed to reduction in the grain size with increasing cobalt content. Smaller grains contain innumerable grain boundaries, and the grain boundaries act as impediments to domain wall motion under an applied alternating field and decrease the initial permeability. In general, an increase in porosity would provide pinning sites, which hinder the domain wall motion [13]. But here, anisotropic contribution of cobalt ions appears to be responsible for the observed decrease in initial permeability.

Anisotropy constant

With increasing cobalt concentration, the value of K1 increases gradually (Table1). Cobalt ions with their unquenched orbital angular moment in octahedral sites give rise to large amount of positive magnetocrystalline anisotropy. Ni-Zn ferrite has small negative magnetic anisotropy arising due to Ni2+ ions at octahedral sites and Fe3+ ions at both octahedral and tetrahedral sites. For 2.5 mol % of cobalt concentration, a small decrease in anisotropy has been noticed due to the fact that the positive contribution of cobalt ions and negative contribution of nickel and iron ions tend to cancel out. As the anisotropy of cobalt ions is very much larger, even for small increase in its concentration enhances the magnetic anisotropy of the ferrite crystal and the same has been reflected in initial permeability.

Electrical properties

The resistivity has been observed to increase throughout the concentration studied and its variation can be explained on the basis of Verwey mechanism [15]. According to this mechanism, the electronic conduction in ferrites is primarily due to hopping of electrons between the ions of the same element present in more than one valence state distributed randomly over crystallographically equivalent lattice sites. The distance between two metal ions in B-sites is smaller than the distance a metal ion at B-site and another metal ion at A-site in ferrites. The electron hopping between B-A sites under normal conditions, therefore, has a very small probability compared to that of hopping between B-B sites. Hopping between A-A sites does not exists for the simple reason due to the absence of Fe2+ ions at A-sites and any Fe2+ ions formed during processing preferentially occupy B-sites only.

In case of zinc containing ferrites volatilization of zinc from the material occurs at high temperatures (~ 1100oC) [16] when heated in air atmosphere. The evaporation of zinc from the material results in cation vacancies and unsaturated oxygen ions [17], affecting the stoichiometry of the material. The excess electrons on oxygen ion then bind with neighbouring Fe3+ ions and leads to the formation of Fe2+ ions in the material in order to satisfy the charge balance in the lattice. Creation of Fe2+ ions gives raise the transfer of electron (electron hopping) between the Fe3+ and Fe2+ ionic states. Also Ni3+ ions are formed during sintering due to considerable absorption of oxygen during cooling cycle from elevated sintering temperatures in oxygen rich regions in sample. Incorporation of larger cobalt ion for smaller nickel ion expands the lattice resulting in a decrease of hopping probability of charge carriers at B-site.The increase in dc resistivity is further substantiated through room temperature Hall voltage measurements at a low field of 1000 Gauss. Hall voltage variations are found to be in accordance with the changes in activation energies. The positive Hall voltages (Table1) signify the electron conduction which supports the above contention.

IV. CONCLUSIONS

Improvements in saturation magnetization and dc resistivity suggest that Ni-Co-Zn ferrite can be used at higher frequencies though anisotropic contribution is substantial in decreasing the initial permeability. Improvement in initial permeability might be possible by choosing a suitable dopant (like Cu or Mg) as an additive to Ni-Co-Zn ferrite system so as to make it an effective core beyond the existing operating frequencies.

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