DIELECTRIC PROPERTIES, RESISTIVITY AND CURIE TEMPERATURE OF Co DOPED CdNi PERMINVAR FERRITE

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ABSTRACT

CdNi perminvar ferrites doped with Co were prepared through the solid-state reaction using conventional ceramic technique. The compositions of the ferrite were $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$ and $Co_{0.02}Cd_{0.28}Cd_{0.28}Ni_{0.50}Fe_{2.2}O_4$. X-ray diffraction study of the samples indicates the single phase of perminvar ferrites. Lattice parameter of the samples was found to be 8.3676 and 8.4249 Å for sample no. (a) of $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$ and sample no. (b) of $Co_{0.02}Cd_{0.28}Ni_{0.50}Fe_{2.2}O_4$, respectively. The porosity of the samples was found to be 10.03 and 9.53%. The values of Curie temperature for the two samples were found to be 472 ± 1 and 405 ± 1^0C, respectively. Resistivity of the samples was measured from room temperature up to 600^0C. At 30^0C resistivity was found to be 334 and 456 ohm-cm, respectively. Frequency dependent dielectric constant for the two samples has been determined from the experimental capacitance values. The value of dielectric constant at frequency, f = 1 kHz and sintering temperature $T_s = 1250^0$C was found to be 16.6×10^6 and 56.1×10^6, for sample no. (a) and (b), respectively. Dielectric constant was observed 3.5 times higher in the Cd rich sample of $Co_{0.02}Cd_{0.28}Ni_{0.50}Fe_{2.2}O_4$ and $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$. Temperature dependent dielectric constant has been measured for the samples in the temperature range of 30 - 250^0C. The value of dielectric constant initially increases slowly with increasing temperature and then rises sharply until reaching a certain temperature, then it begins to decrease with further increase of temperature. Anomalies in the resistivity curves have good consistency with the temperature dependent dielectric constant and Curie temperature values.

INTRODUCTION

NiZn and CdNi ferrite with Co, Cu, Cd, Cr or Mn doping is known as the perminvar ferrite. Normally the permeability of perminvar ferrite is constant in a wide range of frequency.(1) The hysteresis loop is linear in shape at low amplitude of the applied magnetic field and becomes open with increasing the applied magnetic field. At high value of applied magnetic filed the hysteresis loop is similar with those of the usual NiZn and CdNi ferrite. At low magnetic field, Ni-Co perminvar ferrite shows wasp-waisted hysteresis loop when they are cooled in the absence of magnetic field.(1) Taniguchi(2) explained this phenomenon in terms of the fixing of domain walls by local directional order. He considered that if a domain wall exists during the process of cooling, two or more sorts of constituent elements of the ferrite will form a directional order, so as to stabilize the direction of spins in the domain wall. After cooling, the wall is stabilized at its original position, so the magnetization curve starts with low permeability and then jumps to saturation magnetization as soon as the wall gets out of the stabilized position.

Due to high electrical resistivity and low magnetic losses the perminvar ferrite has a great commercial importance of their magnetic properties at high frequency (>1 mHz).[3] A perminvar ferrite is used for high frequency applications up to 100 mHz in broadband transformers, antennas and high quality inductors. It is also used in EMI noise suppression applications for frequencies above 200 mHz.[4] In the practical use of perminvar ferrite, the magnetization is limited in the initial portion of magnetization curve where the permeability is practically constant. This fine quality is destroyed by the application of a strong magnetic field, which may drive out of their stabilized position.[1] Curie temperature of perminvar ferrite is normally >350^0C.[5]

Dielectric behavior is one of the most important properties of ferrites, which markedly depends on the composition, preparation conditions like sintering time and temperature, quantity and type of additives. The study of dielectric properties provides valuable information on the behavior of localized electric charge carriers leading to greater understanding of the mechanism of dielectric polarization in ferrite systems. The dielectric behavior of Nb doped NiZn ferrite was previously studied.[6] They have observed the dielectric constant in the order of > 10^6. The normal dielectric behavior in ferrites is decrease of dielectric constant, K, as the frequency increases. The decrease is rapid at lower frequencies and becomes slow at higher frequencies. The temperature dependence of the dielectric constant, K, at selected frequencies as the temperature increases. This behavior was observed in Ni-Zn, Co-Zn and Mg-Zn ferrites.[7,8] The local displacement of localized electric charge carriers includes dielectric polarization in ferrites.

The present work focuses on the dielectric constant both for temperature and frequency dependent resistivity, density, porosity and Curie temperature of Co doped CdNi perminvar ferrites.

EXPERIMENTAL

CdNi ferrites doped with Co were prepared through the solid-state reaction using conventional ceramic technique. The compositions of the ferrite were $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$ and $Co_{0.02}Cd_{0.28}Ni_{0.50}Fe_{2.2}O_4$. The raw materials Fe_2O_3, NiO and CdO were mixed in a steel ball mill using deionized water for 3 hours then dried and presintered at 900°C for 5 hours. The presintered ferrite powders were crushed and mixed with CoO then wet milled for 6 hours. After drying, the resulting powders were mixed with 1 wt.% polyvinyl alcohol (PVA) as a binder and uniaxially pressed into toroid and pellets at a pressure of 1.2 and 2.2 ton/cm^2, respectively. The compacts were successively sintered in a muffle furnace in air at a temperature of 1250^0C for 2 hours with an intermediate isothermal holding at 600^0C for 4 hours to eliminate the PVA and finally furnace cooled to room temperature.

The bulk density of the pellet samples was determined after sintering at 1250^0C. The single-phase spinel structure of the samples was confirmed by the X-ray diffraction method. The theoretical density of the samples has been calculated using the lattice parameter determined from X-ray data. Dielectric constant of the pellet samples, both for frequency and temperature dependent, have been measured by an Impedance Analyzer, HEWLETT PACKARD, model 4192A. Frequency dependent dielectric constant has been measured up to the frequency of 2 MHz and that temperature dependence at selected frequencies has been measured from room temperature up to 250^{0}C. Resistivity of the pellet samples was measured by the same Impedance Analyzer from room temperature up to 600^{0}C. The Curie temperature of the toroidal samples was determined from the temperature dependence of permeability by an Inductance Analyzer, WAYNE KERR, model 3255B using a laboratory built tubular furnace.

RESULTS AND DISCUSSION

X-ray diffraction study of the samples indicates the single phase of perminvar ferrites. Fig. 1 shows the XRD pattern of two samples, where the indices of the plane are shown in the parenthesis. The bulk density ($d_b = m/v$) was determined from the pellet samples after sintering at 1250^{0}C. The theoretical density ($d_x = 8M/N_a{}^3$) of the samples has been calculated using the lattice parameter, a_0, determined from X-ray data. Porosity, P, of the samples was calculated as $P = (1 - d_b/d_x)$ 100 using the value of theoretical density and the bulk density. All the values of lattice parameter, bulk density, theoretical density and porosity of the samples are listed in Table 1.

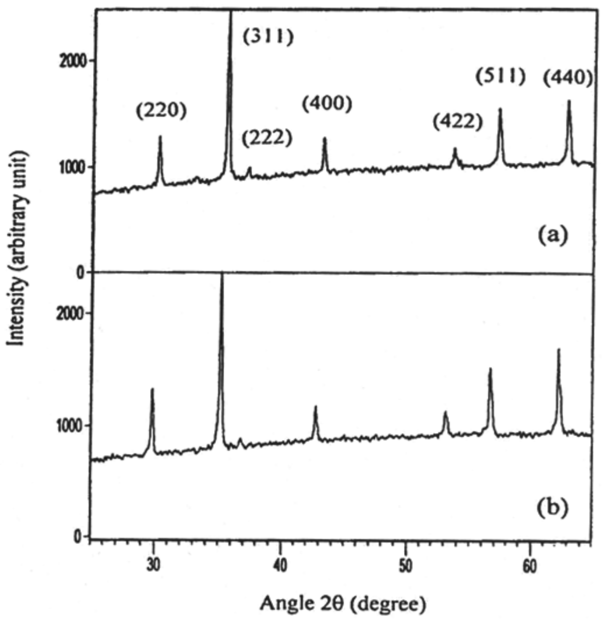


Fig. 1. XRD patterns of (a) $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$ and (b) $Co_{0.02}Cd_{0.28}Ni_{0.50}Fe_{2.2}O_4$ ferrite.

It is observed that the value of lattice parameter was found to be 8.3676 and 8.4249Å for sample no. (a) of $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$ and sample no. of $Co_{0.02}Cd_{0.28}Ni_{0.50}Fe_{2.2}O_4$, respectively. Probably the higher value of lattice parameter (8.4249 Å) for sample no. (b) is due to the higher Cd content and lower Ni content in the sample as the ionic radii of Cd

(0.87 Å) > Ni (0.83 Å).[9] Theoretical density of the samples was determined as 5.58 and 5.56 gm/cc and that of bulk density were found to be 5.02 and 5.03 gm/cc for the two samples. respectively. The porosity of the samples was found to be 10.03 and 9.53%, respectively.

Table 1

Curie temperature, resistivity, dielectric constant, lattice parameter, density and porosity of ferrite samples

Sample	Curie temp. (°C)	Resistivity at 30°C (ohm-cm)	Dielectric constant K at 1 kHz	Lattice parameter ± 0.0004 Å	Theo-retical density (gm/cc)	Bulk density (gm/cc)	Poros ity in (%)
$Co_{0\cdot 02}Cd_{0.20}$ $Ni_{0.58}$ $Fe_{2.2}O_4$	472	334	$16.6x10^6$	8.3676	5.58	5.02	10.03
$Co_{0\cdot 02}Cd_{0.28}$ $Ni_{0.50}$ $Fe_{2.2}O_4$	405	456	$56.1x10^6$	8.4249	5.56	5.03	9.53

Temperature dependence of permeability for the samples has been measured and is shown in Fig. 2 from which the Curie temperatures, T_c, have been determined. The values of Curie temperature were found to be 472±1°C and 405±1°C for sample no. (a) of $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$ and sample no. (b) of $Co_{0.02}Cd_{0.28}Ni_{0.50}Fe_{2.2}O_4$, respectively.

The sharp fall of permeability at the T_c implies the homogeneity and single phase of the studied samples and compatible with the X-ray data. From Fig. 2 it is observed that the Curie temperature decrease with the increase of Cd content and decrease of Ni content. The values of initial magnetic permeability μ' were found to be 230 and 270 for sample nos. (a) and (b), respectively, at room temperature and 1 kHz frequency.

Resistivity of the samples was measured from room temperature up to 600°C. At 30°C resistivity was found to be 334 and 456 ohm-cm for $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$ and $Co_{0.02}Cd_{0.28}Ni_{0.50}Fe_{2.2}O_4$, respectively. Fig. 3 shows the temperature versus resistivity for the two samples of $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$ and $Co_{0.02}Cd_{0.28}Ni_{0.50}Fe_{2.2}O_4$. In the figure, it is clear that the value of resistivity decreases with increasing temperature. This is the behavior of a semiconductor. Ferrite sample exhibits semiconducting character and thus in the present perminvar ferrite resistivity was observed which decreases with increasing temperature up to a certain temperature value 200^0C for both the samples that has a consistency with the temperature dependent dielectric constant curve and will be discussed later. Then the value is almost constant up to value of Curie temperature. Above Curie temperature (472 and 405^0C) for sample nos. (a) and (b), respectively) resistivity was observed which increases with further increase of temperature. This is the behavior of a metal. Probably it shows metallic character above Curie temperature in the present perminvar ferrite.

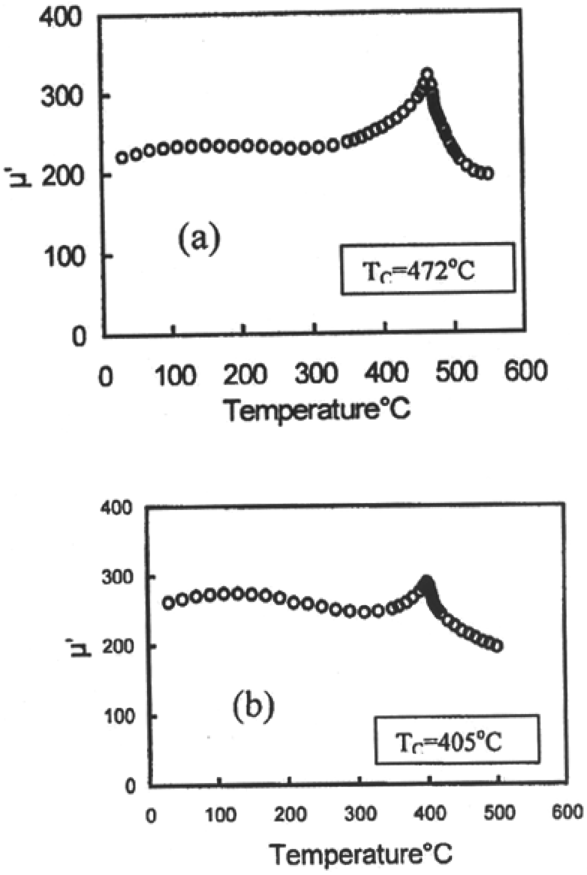
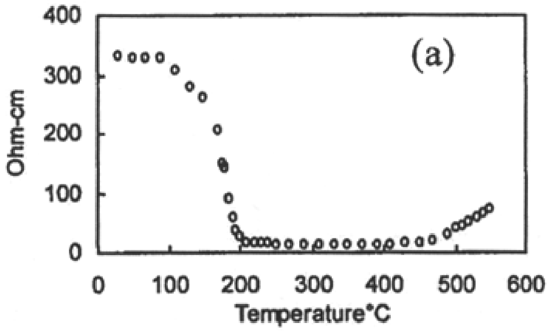


Fig. 2. Temperature versus permeability for sample no. (a) of $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$ and sample $Co_{0.02}Cd_{0.28}Ni_{0.50}Fe_{2.2}O_4$ ferrite.

Frequency dependent dielectric constant for the two samples has been determined from the experimental capacitance values. Dielectric constant, *K*, of the samples has been calculated using the following formula, $K = Cd/\varepsilon_0 A$, where, K = dielectric constant, C = measured capacitance, d = thickness of the sample, ε_0 = a constant with the value of 8.854×10^{-12} $C^2N^{-1}m^{-2}$ and A = area of the circular sample = πr^2, where r is the radius of the sample.[10] Fig. 4 shows the frequency versus dielectric constant at sintering temperature, Ts=1250°C, for sample nos. (a) of $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$ and (b) of $Co_{0.02}Cd_{0.28}Ni_{0.50}Fe_{2.2}O_4$ ferrite. In the figure it is clear that the dielectric constant decreases rapidly with increasing frequency at the lower frequency region from 1 to 100 kHz. This decrease becomes slow at the higher frequency region from 100 kHz to 1 mHz.



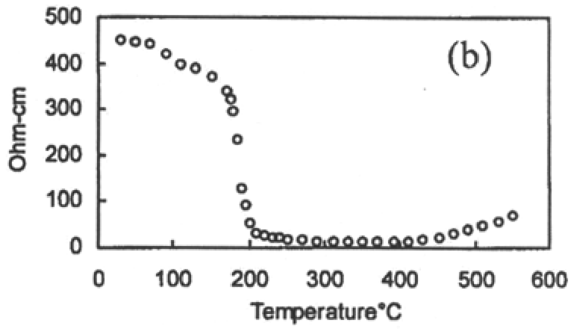


Fig. 3. Temperature versus resistivity curve for sample no. (a) of $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$ and sample no. (b) of $Co_{0.02}Cd_{0.28}Fe_{2.2}O_4$ ferrite.

The decrease of *K* with increasing frequency is a normal dielectric behavior of spinel ferrites. This decrease is rapid at lower frequencies and becomes slow at higher frequencies. In the present case the dielectric constant has been observed to decrease with increasing frequency but the dispersion showed an unusual dielectric behavior similar to that observed by Brockman *et al*[(11)] and Rao *et al*[(6)] in the lower frequency region.

The dielectric constant showed flux reversal accompanying dielectric peak at around 1 mHz. The value of dielectric constant at frequency, f = 1 kHz and sintering temperature T_s = 1250°C was found to be 16.6×10^6 and 56.1×10^6, for sample nos. (a) and (b), respectively. The study of dielectric properties provides information on the behavior of localized electric charge carriers leading to greater understanding of the mechanism of dielectric polarization in ferrite systems. Perminvar ferrite normally shows very high dielectric constant in the order of $>10^6$. The dielectric behavior of Nb doped NiZn perminvar ferrite was previously studied and observed the dielectric constant[(6)] in the order of > $10.^6$ In the present study, dielectric constant was observed in the order of 10^7. Dielectric constant was observed 3.5 times higher in the Cd rich sample of $Co_{0.02}Cd_{0.28}Ni_{0.50}Fe_{2.2}O_4$ than $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$.

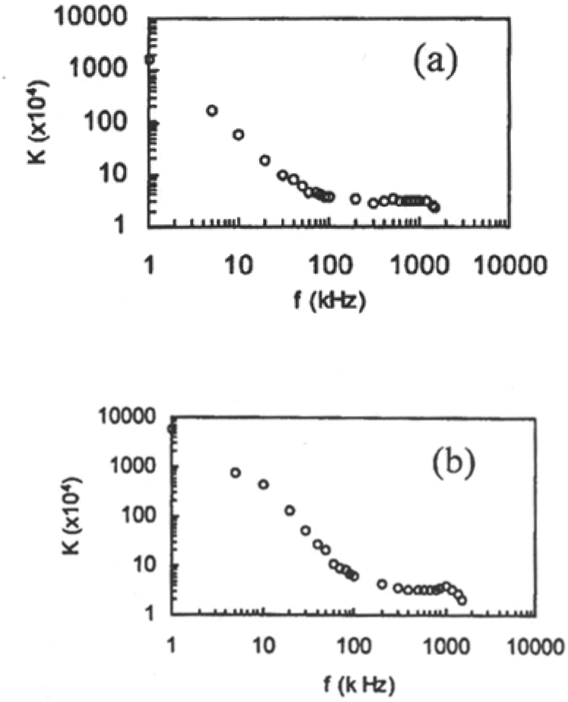


Fig. 4. Frequency versus dielectric constant for sample nos. (a) of $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$ and (b) of $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$ ferrite.

Temperature dependent dielectric constant has been measured for the samples in the temperature range of 30 - 250°C. Fig. 5 shows the temperature versus dielectric constant for sample no. (a) of $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$ and (b) of $Co_{0.02}Cd_{0.28}Ni_{0.50}Fe_{2.2}O_4$ ferrite sintered at 1250°C. The value of dielectric constant initially increases slowly with increasing temperature and then rises sharply until reaching a certain temperature 200°C for both the samples, then it begins to decrease with further increase of temperature. These temperature values at temperature dependent dielectric constant peaks have good consistency with the temperature dependent resistivity curve of Fig. 3, wherein the resistivity curves, anomalies were observed at 200°C for both the samples. There might have some corelation between resistivity and dielectric constant with temperature as the conductivity and the dielectric polarization are of the same origin.

The increase of K with temperature is attributed to the increase in drift mobility of the thermally activated electrons charge carriers according to the hopping conduction mechanism, because the conductivity and the dielectric polarization are of the same origin.

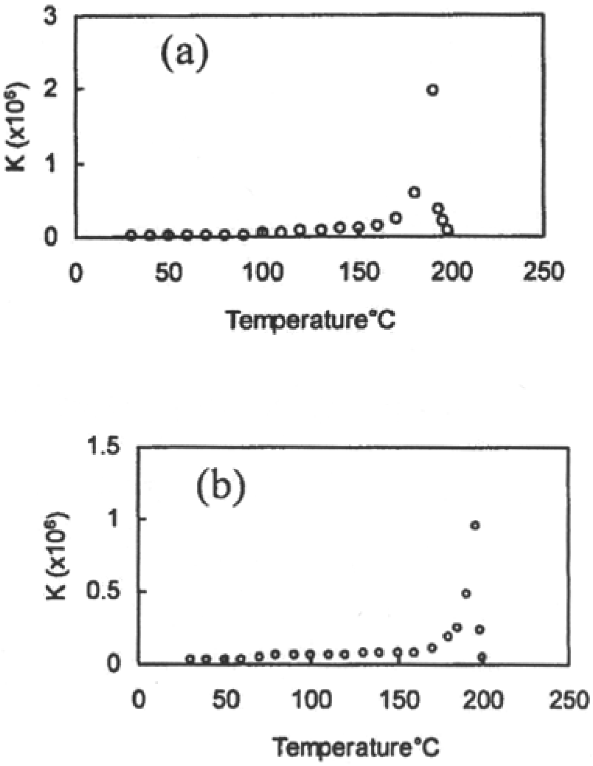


Fig. 5. Temperature versus dielectric constant for sample nos. (a) $Co_{0.02}Cd_{0.20}Ni_{0.58}Fe_{2.2}O_4$ (b) of $Co_{0.02}Cd_{0.28}Ni_{0.50}Fe_{2.2}O_4$ ferrite.

The dielectric behavior in perminvar ferrite can be explained on the basis of the assumption that the mechanism of dielectric polarization is similar to that of conduction. Many scientists established a strong correlation between the conduction mechanism and dielectric constant of ferrite.[12,13] In their studies, they have explained the dielectric behavior 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 displacement of electrons, which determines the polarization, and thus the dielectric constant of ferrite. The trivalent Co ions are expected to enter in the spinel lattice and the accompanying changes could be resulted in conduction mechanism. It is reported that trivalent additions by entering into lattice modify the valence states of iron while producing more Fe^{2+} ions to maintain the charge.[14] The observed higher values of dielectric constants for the Co added perminvar ferrite are in accordance with this.

The dielectric dispersion curve can be explained on the basis of Koops two-layer model and Maxwell-Wagner polarization theory. To interpret the frequency response of dielectric constant in ferrite materials, Koops[15] suggested a theory in which relatively good conducting grains and insulating grain boundary layers of ferrite material can be represented with the behavior of an inhomogeneous dielectric structure, as discussed by Maxwell[(16)] and Wagner.[(17)] Since an assembly of space charge carries in the inhomogeneous dielectric structure described requires finite time to line up their axes parallel to an alternating electric field, the dielectric constant naturally decrease, if the frequency of the reversal field increases. This is in agreement with the observed dielectric dispersion up to 800 kHz.

A good corelation was observed in the Curie temperature, temperature dependent dielectric constant and resistivity data for the two perminvar ferrites. In the resistivity curve, anomalies observed first at 200^0C for both the samples, where in the temperature dependent dielectric constant curves, peaks were observed at the same temperature of 200^0C for the same two samples. The second anomalies in the resistiviry curves were observed at around 470 and 410^0C, where the Curie temperature of the two samples are 472 and 405^0C, respectively. This fact attributed the conductivity and dielectric polarization of the sample to the same origin. Dielectric constant values were observed at kHz frequency in the order of 10^7, which indicates that the samples are perfect perminvar ferrites.

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