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Effect of cobalt substitution on the properties of nickel–copper ferrite

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Abstract

Cobalt-substituted nickel–copper ferrite samples having the chemical formula $\text{Ni}_{0.95-x}\text{Co}_x\text{Cu}_{0.05}\text{Fe}_2\text{O}_4$, where x varies as 0.01, 0.02 and 0.03, were prepared by the standard double sintering ceramic technique. The formation of the ferrite phase was confirmed by x-ray diffraction (XRD) studies. Resistivity and thermo-emf variation with temperature were studied in the temperature range from room temperature to 773 K as a function of cobalt content. As the cobalt content increases, the resistivity of the ferrites decreases. AC conductivity measurements made in the frequency range 100 Hz–1 MHz show that conduction in these ferrites is due to small polaron hopping. The dielectric constant and loss tangent ($\tan \delta$) were measured at room temperature as a function of frequency in the range 20 Hz to 1 MHz. The room-temperature dielectric measurements show dispersion behaviour with increasing frequency. To understand the conduction mechanism, complex impedance measurements were carried out. The variation in saturation magnetization (M_s) with variation of cobalt content is also studied.

1. Introduction

Semiconductor natured polycrystalline spinel ferrites are most important materials due to their interesting electrical properties of low eddy current and dielectric losses. These spinel ferrites find applications in a wide range of frequencies extending from microwave to radio. These are also applicable in many magnetic devices due to the low electrical conductivity as compared to that of magnetic materials. Hence the electrical conductivity, which gives valuable information about the conduction mechanism, is one of the important properties of the ferrites. The order of magnitude of conductivity greatly influences the dielectric and magnetic behaviour of the ferrites and depends on the type of preparation method. In case of the ceramic

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method, it depends on the sintering temperature and time, chemical composition and the kind of substitution [1, 2]. It was reported that ferrites sintered in air are characterized by highly conductive grains separated by highly resistive grain boundaries [3]. The electrical properties are mostly controlled by the grain boundaries. Due to the high electrical resistivity, these ferrites have been extensively used in many magnetic devices than those of soft magnetic alloys. The hopping mechanism of conduction was described by Verwey [4] for the first time. Several researchers have incorporated various substitutions and studied the magnetic, dielectric and thermal properties of ferrites such as Ni–Co [5] and Ni–Cu mixed ferrites [6, 7] to achieve the desired dielectric, thermal and magnetic properties [8]. The copper ferrite, having interesting electric and magnetic properties, is distinguished from the other ferrites by the fact that it undergoes a structural phase transition accompanied by a reduction in the crystal symmetry due to the co-operative Jahn–Teller effect. Van Uitert [9] noticed that a very large increase in the room-temperature (RT) resistivity of nickel ferrite is achieved by substituting one or two per cent of Co ions. This has been subsequently confirmed by Wu *et al* [10] and Parker *et al* [11]. In the present work, we report the electrical resistivity, AC conductivity, dielectric constant and complex impedance measurements along with magnetic properties of $\text{Ni}_{0.95-x}\text{Co}_x\text{Cu}_{0.05}\text{Fe}_2\text{O}_4$ ferrites.

2. Experimental details

2.1. Preparation

Polycrystalline ferrites having the general formula $\text{Ni}_{0.95-x}\text{Co}_x\text{Cu}_{0.05}\text{Fe}_2\text{O}_4$ (where $x = 0.01, 0.02$ and 0.03) were prepared by the conventional double sintering ceramic technique, starting with AR grade NiCO_3 , CoCO_3 , CuCO_3 and Fe_2O_3 . The starting materials were mixed thoroughly in required molar proportions and presintered at 1073 K for 12 h in air. The presintered mixture was ground and pressed in the form of pellets having 2–3 mm thickness and 15 mm diameter. The samples were finally sintered at 1423 K for 12 h in air and furnace cooled.

2.2. Phase identification

X-ray diffraction (XRD) studies of the samples were carried out using a Philips PW-3710 x-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The morphological features were observed with a scanning electron microscope (SEM: model JEOL-JSM 6360).

2.3. Characterization

The variation of DC resistivity with temperature (RT to 773 K) was measured by the two-probe method. The Seebeck coefficient (α) was measured by the differential method in the same temperature range by maintaining a thermal gradient of 25 °C across the sample.

The frequency dependence of capacitance and dissipation factor ($\tan \delta$) in the range 20 Hz to 1 MHz was studied using a precision LCR meter bridge (model HP 4284 A). The AC conductivity was calculated using room-temperature dielectric data. The complex impedance measurements were made using the same equipment. The real (Z') and imaginary (Z'') parts of the complex impedance at room temperature were measured as a function of frequency using the samples having the same thickness (i.e. 2 mm) and diameter (i.e. 15 mm) in the same frequency range. A high-field hysteresis loop tracer, consisting of an electromagnet working on 50 Hz mains frequency, was used to measure the saturation magnetization (M_s) and coercive field (H_c) of the sample.

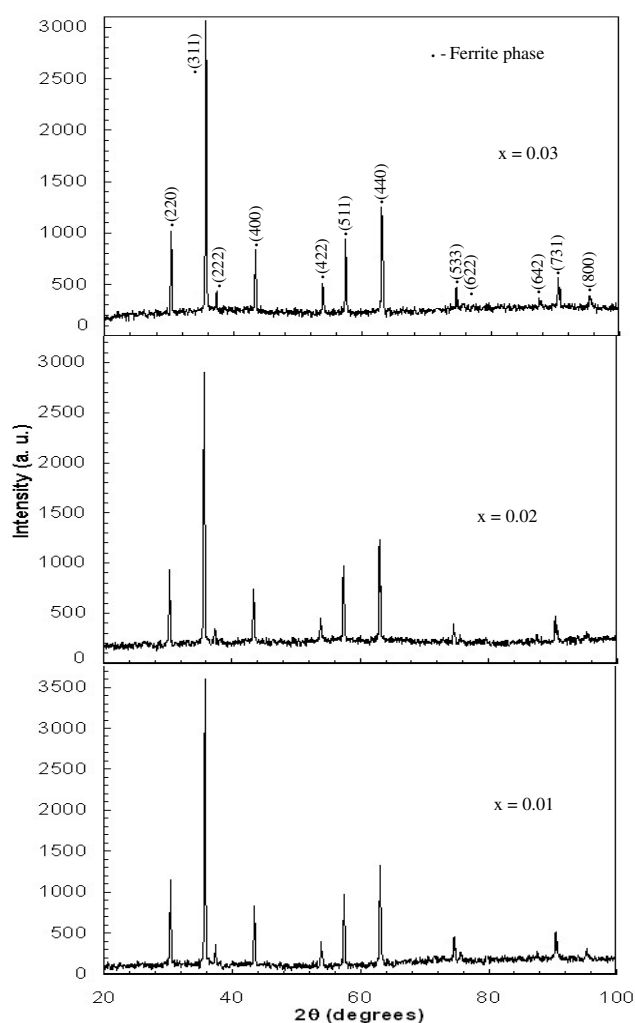


Figure 1. XRD patterns of $\text{Ni}_{0.95-x}\text{Co}_x\text{Cu}_{0.05}\text{Fe}_2\text{O}_4$ ferrites.

3. Result and discussions

3.1. Phase identification

X-ray diffraction patterns of the samples with $x = 0.01, 0.02$ and 0.03 are shown in figure 1. The samples have a cubic spinel structure. The lattice parameter varies between 8.32 and 8.34 Å with increasing Co content. This variation can be ascribed to the difference in ionic sizes of the component ions. The Co^{2+} ions have larger ionic radius (0.82 Å) than Ni^{2+} (0.78 Å), Cu^{2+} (0.70 Å) and Fe^{3+} (0.67 Å) ions.

The SEM micrographs of ferrite samples are shown in figure 2. The average grain size was calculated by Cottrell's method. As reported earlier [12], the observed grain size increases slightly with the addition of cobalt. The average grain sizes for the samples with $x = 0.01, 0.02$ and 0.03 are $1.16, 1.28$ and 1.32 μm , respectively. The increased grain size results in an increase of mean free path of the electrons and hence causes the change in resistivity.

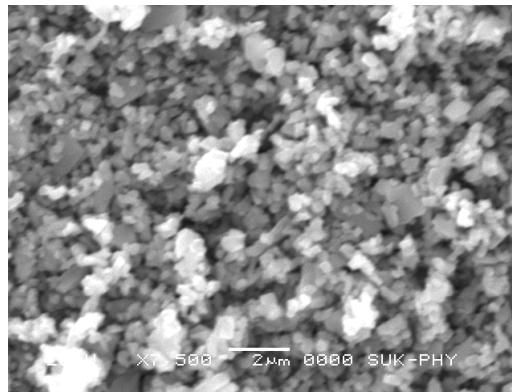
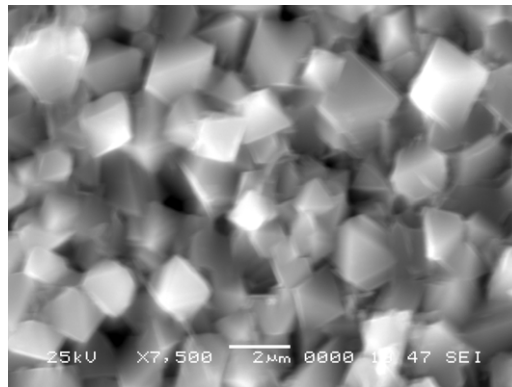
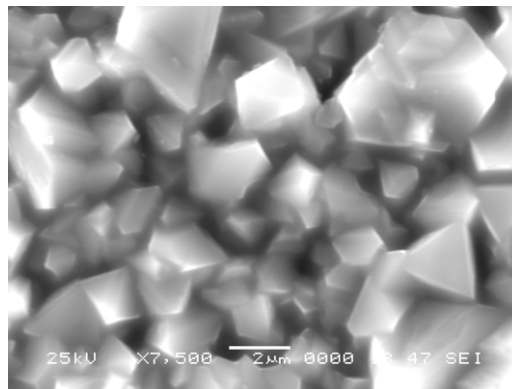
**(a)****(b)****(c)**

Figure 2. SEM micrographs of (a) $x = 0.01$, (b) $x = 0.02$ and (c) $x = 0.03$ ferrite.

3.2. Electrical measurements

Figure 3 shows the variation of DC resistivity with temperature. It is observed that the resistivity decreases linearly with increasing temperature, reflecting the semiconducting nature of the ferrites. The conduction mechanism in ferrites is explained on the basis of the Verwey

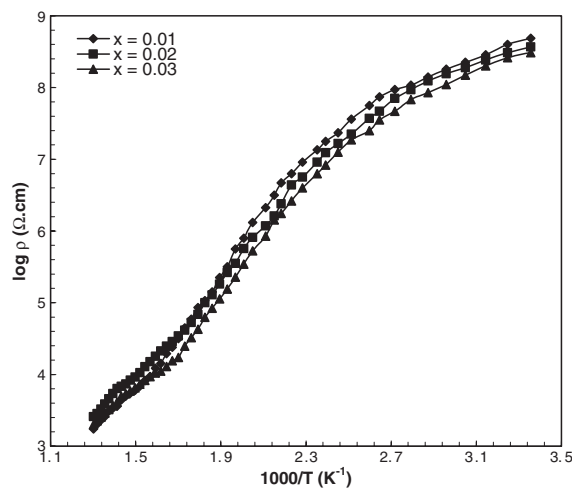


Figure 3. Variation of DC resistivity of $\text{Ni}_{0.95-x}\text{Co}_x\text{Cu}_{0.05}\text{Fe}_2\text{O}_4$ with temperature.

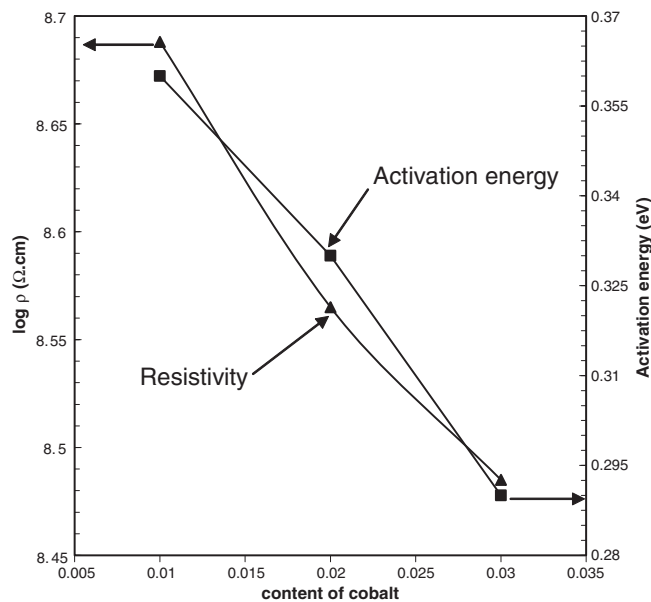


Figure 4. Variation of room-temperature DC resistivity and activation energy with cobalt content.

de Boer [13] mechanism that involves exchange of electrons between the ions of the same elements present in more than one valence state and distributed randomly over equivalent crystallographic lattice sites. The decrease in resistivity with temperature is due to the increase in drift mobility of the charge carriers. Also, conduction in ferrite is attributed to hopping of electrons from Fe^{3+} to Fe^{2+} ions [14]. The number of such ion pairs depends upon the sintering conditions and amount of reduction of Fe^{3+} to Fe^{2+} at elevated temperatures. The resistivity of ferrite is controlled by the Fe^{2+} concentration on the B-site.

The variation of room-temperature DC resistivity with cobalt content is shown in figure 4. The decrease in DC resistivity may be attributed to changes in cation distribution, formation of

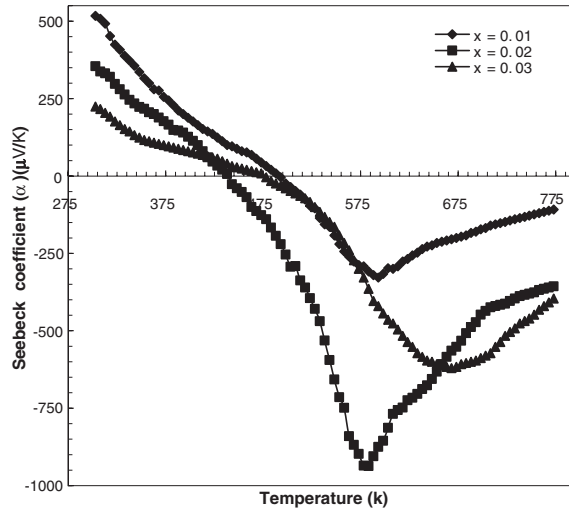


Figure 5. Variation of Seebeck coefficient of $\text{Ni}_{0.95-x}\text{Co}_x\text{Cu}_{0.05}\text{Fe}_2\text{O}_4$ with temperature.

excess Fe^{2+} ions and the difference in ionic size of the cations. Due to the higher ionic size of Co as compared to Ni, Cu and Fe, its addition distorts the ferrite lattice. The distortions can affect the motion of charges causing a change in resistivity [10].

In ferrites, the electrons are localized and there is little overlap between the wavefunctions of ions situated on adjacent sites. In the presence of lattice vibrations, the ions occasionally come so close that the transfer of electrons from one ion to another occurs with high probability. Hence the mobility is temperature dependent and is characterized by activation energy. The activation energy in the present case was obtained by fitting the DC resistivity data with the Arrhenius relation

$$\rho = \rho_0 \exp(\Delta E/kT), \quad (1)$$

where ΔE is the activation energy and k is the Boltzmann constant. The lowering of activation energy in the ferrimagnetic region is attributed to the effect of spin disordering [3]. It is well known that the electron and hole hopping between the $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{Ni}^{3+}/\text{Ni}^{2+}$, $\text{Cu}^{2+}/\text{Cu}^{1+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ ions, with an activation energy ≈ 0.2 eV, is responsible for electrical conduction in mixed ferrites [15]. The present values of activation energies suggest that the hopping of small polarons is responsible for the conduction in the present samples.

The compositional variation of the Seebeck coefficient as a function of temperature is shown in figure 5. All the samples show a p-type to n-type transition. A negative value of α confirms n-type charge carriers and a positive value confirms p-type charge carriers. The most probable mechanism for n-type conduction is electron hopping between Fe^{3+} and Fe^{2+} ions [13, 16], such as



The hole exchange between Ni^{3+} and Ni^{2+} , Cu^{2+} and Cu^{1+} and Co^{3+} and Co^{2+} ions is responsible for p-type charge carriers [13]. The coupling mechanism for hole exchange can be represented as



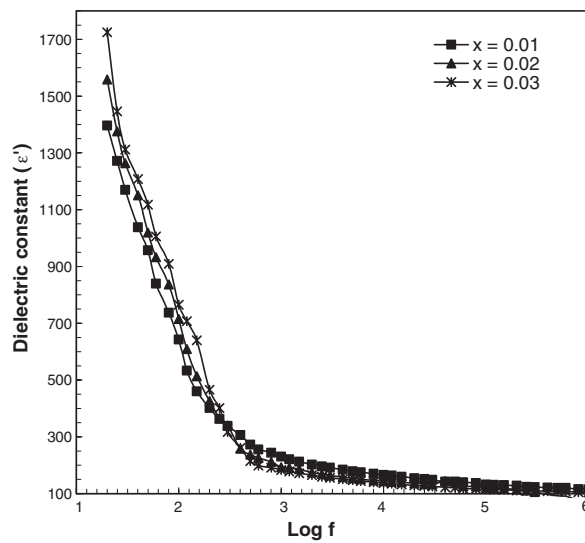


Figure 6. Variation of dielectric constant of $\text{Ni}_{0.95-x}\text{Co}_x\text{Cu}_{0.05}\text{Fe}_2\text{O}_4$ with frequency.

and



In general, a small value of α ($\leq 30 \mu\text{V K}^{-1}$) indicates that the electronic state is metallic, while large values of α ($\geq 100 \mu\text{V K}^{-1}$) are related to localized electronic states for the oxide ceramics [17]. The values of α obtained in the present system are much greater than $100 \mu\text{V K}^{-1}$, indicating polaron hopping type of conduction.

3.3. Dielectric properties

The effect of frequency on the dielectric constant and dielectric loss factor is illustrated in figures 6 and 7 respectively. The dielectric constant is found to decrease at lower frequencies and remains constant at higher frequencies, showing the usual dielectric dispersion. The dispersion of dielectric constant with frequency is due to Maxwell–Wagner [18, 19] type interfacial polarization in agreement with Koop's phenomenological theory [20].

According to Rabinkin *et al* [21], the polarization in ferrite is through a mechanism similar to the conduction process. The presence of Fe^{3+} and Fe^{2+} ions have rendered ferrite materials dipolar. Rotational displacement of dipoles results in orientational polarization. In ferrites, rotation of $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ dipoles may be visualized as the exchange of electrons between the ions so that the dipoles align themselves in response to the alternating field. The existence of inertia to the charge movement would cause relaxation of the polarization. The polarization at lower frequencies may result from electron hopping between $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ ions in the ferrite lattice. The polarization decreases with increase in frequency and reaches a constant value due to the fact that beyond a certain frequency of external field the electron exchange $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ cannot follow the alternating field [15]. In the present system, the presence of $\text{Ni}^{3+}/\text{Ni}^{2+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ ions gives rise to p-type carriers. The local displacement of p-type carriers in the direction of an external electric field also contributes to net polarization in addition to that of the n-type carriers. However, the contribution due to p-type carriers should be smaller than the electronic exchange between $\text{Fe}^{3+}/\text{Fe}^{2+}$ and has an opposite sign. Since the mobility of p-type

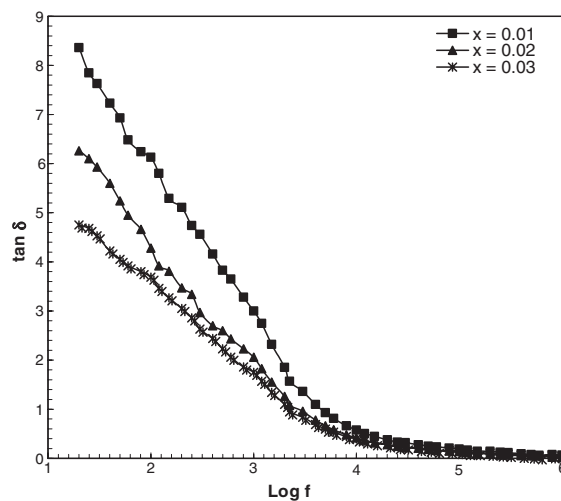


Figure 7. Variation of loss tangent of $\text{Ni}_{0.95-x}\text{Co}_x\text{Cu}_{0.05}\text{Fe}_2\text{O}_4$ with frequency.

carriers is smaller than n-type carriers, their contribution to the polarization decreases more rapidly even at lower frequencies. As a result the net polarization increases initially and then decreases with increase in frequency, as is observed in the present system. Similar results were reported earlier by Popandian *et al* [15].

Iwauchi [22] and Rezlescu *et al* [8] have established a strong correlation between the conduction mechanism and dielectric behaviour of ferrites. The electronic exchange in these ferrites results in the local displacement of charges in the direction of the applied field, which determines the polarization of the ferrites. As both electrical conductivity and dielectric behaviour are transport properties and their variation with composition is similar, it may be presumed that the same mechanism is responsible for these phenomena. The resistivity and dielectric constant show an inverse trend of variation with cobalt content due to their inverse interdependence.

The variation of $\tan \delta$ with frequency shows a similar nature as the variation of ϵ' with frequency. The loss factor is considered to be caused by domain wall resonance. At higher frequencies, losses are found to be low since domain wall motion is inhibited and magnetization is forced to change by rotation.

To understand the conduction mechanism and the type of polarons responsible for conduction, the variation of AC conductivity as a function of frequency is represented in figure 8. It is well known that AC conductivity in disordered solids is directly proportional to frequency. The electrical conduction mechanism in terms of the electron and polaron hopping model has been discussed earlier by Austin and Mott [23]. The plots of AC conductivity are linear, indicating that the conduction is due to small polarons. However, a slight decrease in conductivity at certain frequencies is attributed to mixed polaron (small and large) conduction [5]. The frequency-dependent conduction is attributed to small polarons, as reported by Alder and Fienleib [24]. At higher frequencies, where conductivity increases greatly with frequency, the transport is dominated by contributions from hopping infinite clusters.

3.4. Complex impedance

Typical room-temperature complex impedance spectra for the samples with $x = 0.01, 0.02$ and 0.03 are shown in figures 9(a)–(c). In the present investigation a well resolved semicircle

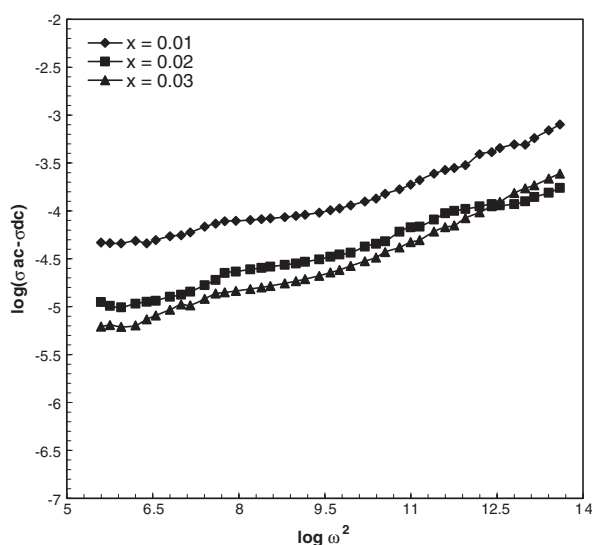


Figure 8. Variation of AC conductivity of $\text{Ni}_{0.95-x}\text{Co}_x\text{Cu}_{0.05}\text{Fe}_2\text{O}_4$ with frequency.

is observed for each sample between the frequency range 20 Hz–1 MHz. The size of the semicircle changes with grain size. The presence of a single semicircular arc obtained at higher frequencies corresponds to electrical conduction by the interior of the bulk grain. The diameter of the semicircle corresponds to the resistance of the grain [25]. As the cobalt content increases, the diameter of the semicircle decreases, indicating a reduction of the grain interior resistance. The observed semicircle can be modelled by an equivalent circuit consisting of a parallel combination of bulk resistance (R_g) and bulk capacitance (C_g), which is shown in the inset of figure 9(a). This RC equivalent circuit accurately fits each Cole–Cole semicircle. The fitting procedure used here is similar to the one described by Kleitz *et al* [26].

The real (Z') and imaginary (Z'') parts of the complex impedances were calculated using the following equations [27]:

$$Z = Z' - jZ'' \quad (6)$$

$$Z' = \frac{R_g}{1 + R_g^2 \omega^2 C_g^2} \quad (7)$$

$$Z'' = \frac{R_g^2 \omega C_g}{1 + R_g^2 \omega^2 C_g^2} \quad (8)$$

where ω is the angular frequency. The impedance plot corresponding to calculated values of Z' and Z'' are shown by open squares (figures 9(a)–(c)). The observed and calculated complex impedance data match each other fairly well.

3.5. Hysteresis measurements

Typical magnetic hysteresis loops for $\text{Ni}_{0.95-x}\text{Co}_x\text{Cu}_{0.05}\text{Fe}_2\text{O}_4$ ferrites are shown in figures 10(a)–(c). Figure 11 shows the variation of saturation magnetization and coercive field with cobalt content. The saturation magnetization of the samples decreases with decrease in cobalt concentration. This may be due to the relatively high orbital contribution of Co^{2+} ions to the magnetic moment, which gives large induced anisotropy. The surface spin disorder due

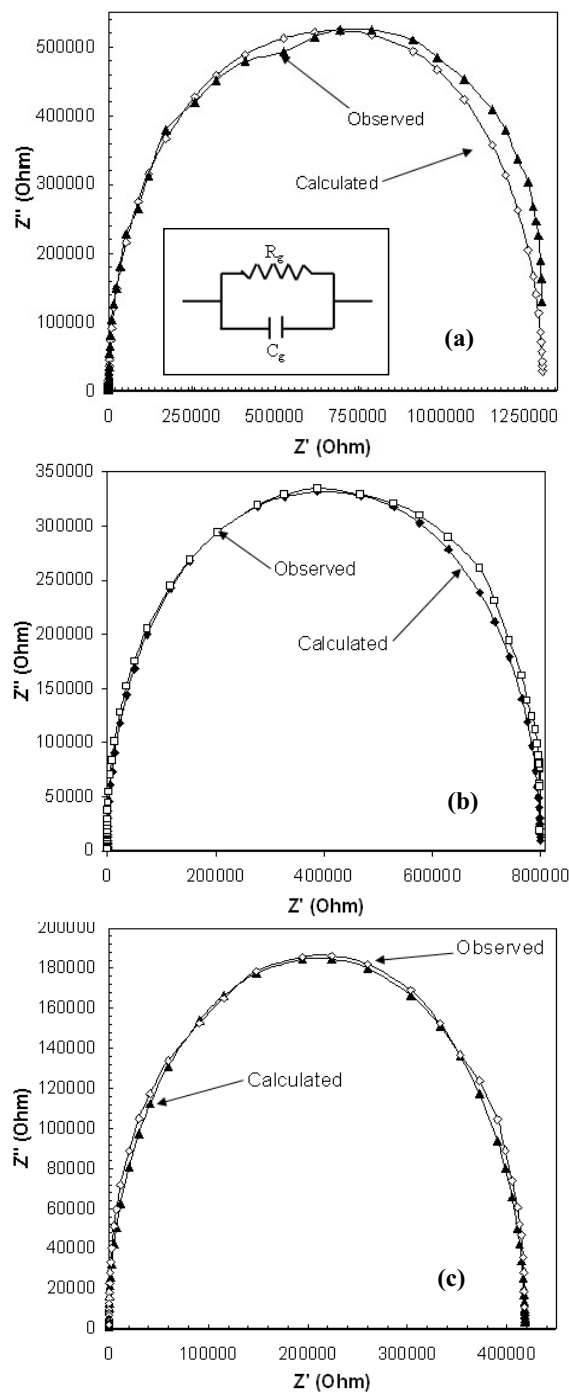


Figure 9. Variation of complex impedance for (a) $x = 0.01$, (b) $x = 0.02$ and (c) $x = 0.03$ at room temperature.

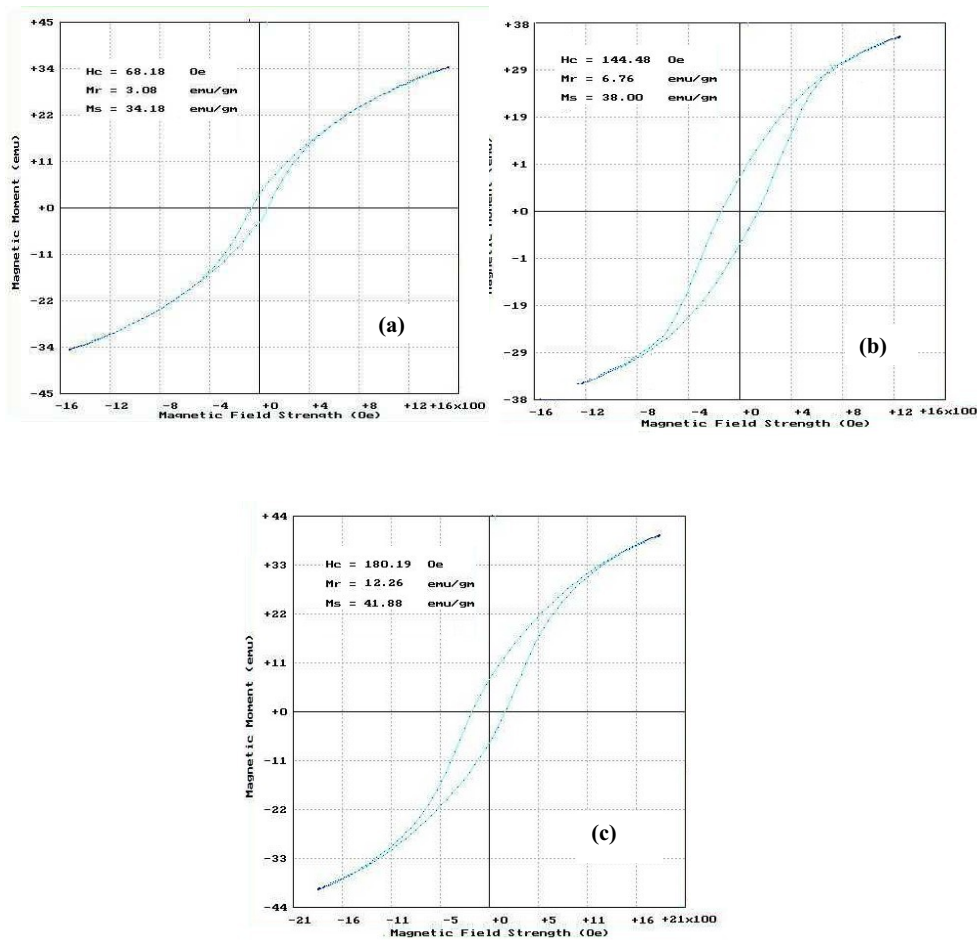


Figure 10. Hysteresis loops for the samples (a) $x = 0.01$ (b) $x = 0.02$ and (c) $x = 0.03$.

to broken exchange bonds, high anisotropy layer and loss of long-range order in the surface layer are strong in the case of nickel ferrite due to super-exchange interaction through the oxygen ions [28]. In ferrites two magnetic ions are separated by a nonmagnetic ion (in this case oxygen); hence magnetic ions have a magnetic interaction mediated by the electrons in their common nonmagnetic neighbours, which is more important than their direct exchange interactions referred to as super-exchange interaction. The presence of ions in the form of impurity or an absence of the oxygen ions at the surface leads to breakage of super-exchange bonds between magnetic cations, inducing a large surface spin disorder [29]. In the mixed spinel-type structure, some Ni^{2+} ions may occupy tetrahedral sites and hence the net magnetization should be higher than that for the inverse spinel structure as the magnetic moment of Ni^{2+} ($3.0 \mu_B$) at the A-site is smaller than magnetic moment of Fe^{3+} ($5.0 \mu_B$) [30]. However, the low values of saturation magnetization obtained in the present work suggest that the mixed spinel structure is not likely to be present in our case.

Another important factor which influences the magnetization of ferrite is the microstructure. The individual grains act as magnetic material having a certain amount of

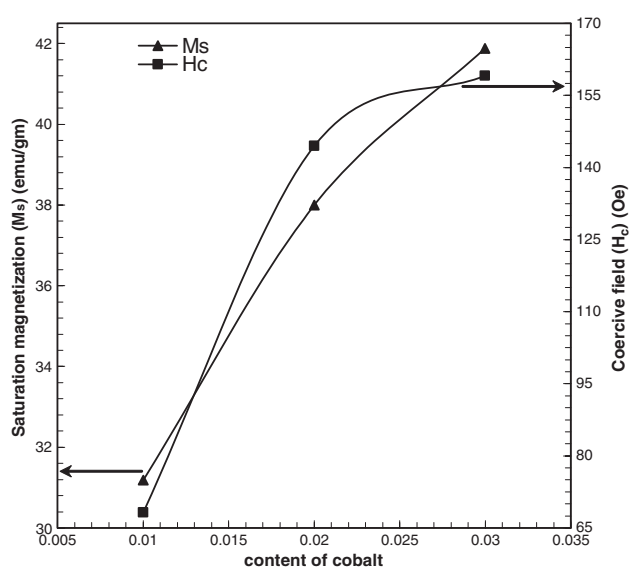


Figure 11. Variation of saturation magnetization and coercive field with cobalt content.

saturation magnetization. These grains form a magnetic circuit to produce resultant saturation magnetization. The presence of pores breaks the magnetic circuits present among the grains and results in a net reduction of magnetic properties with increasing pore concentration [31]. In the present report, the average grain size of the ferrite phases goes on increasing with cobalt content and results in a decrease in porosity; as a consequence, the saturation magnetization increases. The coercive force goes on increasing with increased cobalt content (figure 11). This is attributed to the fact that the coercivity (H_c) is directly proportional to the magneto-crystalline anisotropy constant. A small number of Co^{2+} ions enter into the spinel lattice, leading to the appearance of the spin-orbital coupling which determines the magnetic anisotropy in the ferrites. Therefore as the cobalt content increases, the magneto-crystalline anisotropy increases, which in turn decreases the domain wall energy resulting in high coercive force.

4. Conclusion

Polycrystalline spinel ferrites $\text{Ni}_{0.95-x}\text{Co}_x\text{Cu}_{0.05}\text{Fe}_2\text{O}_4$ were prepared by the conventional double sintering ceramic method. Due to the change in average grain size with the cobalt content, a variation in grain boundary volume and porosity was observed, which causes a variation in the resistivity. As the grain size increases, the resistance of the grain diminishes as a consequence of the increase in mean free path into the grains. The maximum resistivity is obtained for a composition with $x = 0.01$ composition. In future the maximum magnetoelectric output can be obtained by incorporating the $x = 0.01$ compositional ferrite phase in the ferroelectric phase which has high piezoelectric coefficient. The values of the Seebeck coefficient (α) and the AC conductivity measurements suggest that the conduction may be due to the polaron hopping mechanism. The dielectric dispersion with frequency was observed, and this has been explained on the basis of an electron-hole hopping mechanism, which is responsible for conduction and polarization. Since the dielectric constant is inversely proportional to the resistivity, it shows a decreasing trend with increasing cobalt content. Impedance spectroscopy allowed us to study the influence of grain size in the impedance

response of polycrystalline (NiCoCu)ferrite. The complex impedance spectra suggest a grain interior contribution in the conduction process. The oxygen ion conduction dominates over all conduction processes with increase in temperature. The magneto-crystalline anisotropy increases with increased cobalt content, which contributes to the increase in saturation magnetization. The hysteresis behavior suggests that these ferrites are useful in phase shifters.

Acknowledgment

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