

Influence of Cr³⁺-ions Substitution on the Magnetic Properties and Electrical Resistivity of Ni-Cu-Zn ferrites

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Abstract: The standard ceramic method was used to prepare NiCuZn ferrites powders with chemical formula of Ni_{0.4}Cu_{0.2}Zn_{0.4}Cr_xFe_{2-x}O₄ (x = 0 to x = 0.15 with step = 0.025). The effect of Cr-substitution on the structure, magnetic properties and dc electrical resistivity has been studied. X-ray patterns indicated the presence of a single spinel phase for all investigated samples. SEM micrographs revealed that the average grain size decrease with Cr substitution. VSM was used to measure the magnetization at room temperature. The initial permeability was measured, on toroidal samples used as transformer cores, as a function of temperature at constant frequency of 10 KHz and Curie temperature (T_c) was determined. It was found that the magnetization, the initial permeability and Curie temperature decreased with increasing Cr-content. Whereas, dc resistivity increased with increasing Cr-concentration. The obtained results were discussed in the light of domain theory and ion pair model.

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1. Introduction:

Recently, NiCuZn ferrites have been extensively studied for multilayer chip inductor (MLCI) applications because of their good properties at high frequencies and low sintering temperatures [1-3]. For optimum performance of MLCIs with high inductance and reliability, high permeability NiCuZn ferrites are required. There are several routes to increase the permeability values of such ferrites, as, increasing grain size, increasing magnetization or decreasing magnetostriction constant through the incorporation of some cations [4, 5]. The magnetic properties of the ferrite are highly sensitive to the technology parameters, especially to the amount of constituent metal oxides or additives in their compositions [6]. The effect of substituting trivalent ions for iron in ferrites has been investigated [7, 8]. It was found that, the Al³⁺-ion substitution improved the magnetic properties by increasing the values of magnetization, initial permeability and Curie temperature for MnNiZn ferrites [9]. Bhosale et al.[10] studied the effect of Al³⁺-ion substitution in the system Ni Al_x Fe_{2-x} O₄ and they found that the net magnetization decreased, the domain state changed from single domain to multi domain and the Curie temperature decreased as Al content increased. Whereas, Masti et al. [11] studied the effect of Cr³⁺-ion substitution in the system Cd_x Mg_{1-x} Cr_y Fe_{2-y} O₄ and they found that both the saturation magnetization and initial permeability decreased with increasing the Cr³⁺-ion content. Many research efforts have devoted for studying NiCuZn ferrites, especially to realize the best possible concentrations that compromise the

electrical and magnetic properties [12-16]. It was reported that the optimum bulk density, initial permeability and dc electrical resistivity can obtained at copper concentration 0.2 [17]. As well as Zn concentration 0.4 is corresponding to maximum magnetization [18]. In previous work[19], the effect of Al³⁺ substitution in NiCuZn ferrites had been studied and it was found that Al ions improve the magnetization as well as the initial permeability with no considerable effect on T_c. In the present work, our efforts continue to investigate the effect of Cr³⁺- ion substitution on the structure, magnetic properties and dc electrical resistivity of Ni_{0.4} Cu_{0.2} Zn_{0.4} Cr_x Fe_{2-x} O₄ ferrites.

2-Experimental procedure:

Samples with the chemical formula Ni_{0.4} Cu_{0.2} Zn_{0.4} Cr_x Fe_{2-x} O₄ (x =0 to x = 0.15 with step = 0.025) were prepared by using standard ceramic technique. High purity oxides, 99.9% of NiO, CuO, ZnO, Cr₂O₃ and Fe₂O₃ were mixed together according to their molecular weights. The mixture of each sample was ground to a very fine powder and then presintered at 900°C for 12 h in one cycle. The presintered mixture was ground again and pressed at room temperature into discs and toroids. They were finally sintered at 1200°C for 5h and then slowly cooled to room temperature. X-ray diffraction (XRD) patterns were performed using diffractometer of type x'pert Graphics identify with CuK_α radiation. The porosity percentage (P %) was calculated for all samples according to the relation P% =100 [1 - (d/d_x)] %. Where d_x is the theoretical x-ray density of samples which calculated using the formula d_x =

$8M/Na^3$ (M is the molecular weight, N is Avogadro's number and a is the lattice parameter) and d is the density of each composition measured in distilled water using Archimedes principle. The microstructure was investigated using scanning electron microscope (SEM) of type (JEOL JSM5600). The magnetization M (emu/g) is measured at room temperature in the magnetizing field H (Oe) ranged from zero to 6000 Oe using the LDJ vibrating sample magnetometer (VSM) model 9600. The initial permeability (μ_i) was measured as a function of temperature at constant frequency ($f = 10$ kHz) and low magnetizing current of $I_p = 10$ mA. The value of μ_i was calculated using poltinnikov's formula [20], which is given by $V_s = K\mu_i$, $K = 0.4\pi N_p N_s I_p A \omega / L$ where V_s is the induced voltage in secondary coil, N_p and N_s are the number of turns of primary and secondary coils, respectively. A is the cross-sectional area

3- Results and Discussion:

3.1 X-ray and Porosity:

XRD patterns for all investigated samples are shown in Fig.1. They confirmed the formation of the single spinel phase. The values of d -spacing are calculated according to Bragg's law and hence the average lattice parameter a (\AA) is calculated. The variation of a (\AA) with the Cr-concentration is plotted in Fig.2. It is clear that as Cr-concentration increases the lattice parameter decreases almost linearly obeying Vegard's law. Similar behavior was observed in Cr-substituted lithium ferrite [21, 22], cobalt ferrite [23] and nickel ferrites [24]. The decrease in lattice parameter with increasing Cr-concentration is due to the difference in the ionic radius of the substituent Cr^{3+} (0.63\AA) and Fe^{3+} (0.645\AA) [25].

Scanning electron microscope (SEM) images for etched samples (using boiling Aqua Regia) with Cr contents ($x=0.0, 0.05, 0.1$ and 0.15) are shown in Fig. 3. It is clear that, as Cr-content (x) increases the average grain size decreases. This behavior is in agreement with the behavior reported in [26]. The average grain diameter (D) of each sample was determined using main linear intercept method by drawing random lines on the obtained photographs and counting the number of grain boundaries [27]. The average grain size (m) was calculated by dividing the length of the straight line over the number of grain boundaries. The composition dependence of D is illustrated in the inset of fig. 2. The variation of porosity with Cr-concentration is illustrated in fig. 2. The shown behavior reveals the decrease of porosity with increasing Cr content. The well known sources of porosity in ceramic samples are intragranular porosity (P_{intra}) and intergranular porosity (P_{inter}) [28]. Furthermore, it was reported that the intergranular porosity (P_{inter}) is directly proportional to the grain size [29, 30]. It was found

that, as Cr-concentration increases the grain size decreases. Thus, the decrease of $P\%$ with increasing Cr-content could be attributed to the decrease of intergranular porosity (P_{inter}) indicating that P_{inter} plays the main role in the value of porosity ($P\%$).

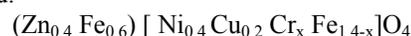
3.2. Magnetization:

Fig.4 illustrates the variation of magnetization M (emu/g) as a function of applied magnetic field H (Oe) at room temperature. As a normal behavior, the magnetization increases with increasing applied magnetic field and attain its saturation around applied field $H=0.2T$ as a soft magnetic material. The composition dependence of saturation magnetization is shown in Fig.5. It is clear that as Cr-concentration increases M_s decrease (almost linear). For spinel structure, the magnetizations of tetrahedral site (A-site) and octahedral one (B-site) are in opposite directions. Thus, the total magnetization could be expressed as:

$$M = M_B - M_A \quad (1)$$

Where, M_A and M_B are the magnetic moments of A and B-sites respectively [31]. Since Cr^{3+} , Ni^{2+} , and Cu^{2+} ions preferably occupy B-site [31-33] in addition to the highly preference of Zn to occupy A-site [18].

Therefore, the following cation distribution is assumed.



Considering the magnetic moment values of each cation in our system, and in view of both equation (1) and the assumed cation distribution, the net magnetic moment per molecular formula could be employed to estimate the following equation

$$M = (5-2x) M_B \quad (2)$$

Equation 2 indicates that the magnetic moment per molecular formula decreases linearly with Cr-ion concentration x . This behavior fits well with the obtained experimental results shown in fig. 5.

3.2 Initial Permeability and Curie temperature:

The temperature dependence of initial permeability (μ_i) for all samples is shown in fig.6. It is found that the curves are typical of multi domain grains showing a sudden drop in the values of μ_i at the Curie temperature T_c , which is determined at the rapid decrease of μ_i . The dependence of both the initial permeability μ_i at room temperature and T_c on the Cr-concentration are shown in Fig.7. The figure enlighten that, as Cr-concentration increases μ_i decreases. The behavior of μ_i could be explained in view of the approximate equation for initial permeability [34].

$$\mu_i \cong \left(M_s^2 D / \sqrt{K_1} \right) \quad (3)$$

Where M_s is the saturation magnetization, K_1 is the magneto crystalline anisotropy constant and D is the average grain size. It is known that the anisotropy

field in ferrites results from the presence of Fe^{2+} ions which formed during the sintering process [35, 36]. Hence, the Fe^{2+} -ion has a large magnetic anisotropy due to its strong spin-orbit interaction of the 3d orbital in comparison to weak anisotropy energy of Fe^{3+} ions because its orbital angular momentum is zero [37]. Therefore, increasing Cr^{3+} ions content leads to decrease the anisotropy constant due to the relative reduction in Fe^{2+} ion concentration. The decrease of μ_i with Cr-concentration is attributed to the decrease of M_s and D even the value of K_1 decreases. This means that the decrease of both M_s and D with Cr-concentration have the dominant effect.

Fig.7 shows also that the Curie temperature decreases with increasing Cr-concentration. The main factor that affects the value of T_c is the A-B interaction [18]. The decrease in the distance between the moments of A and B sites as noticed from lattice

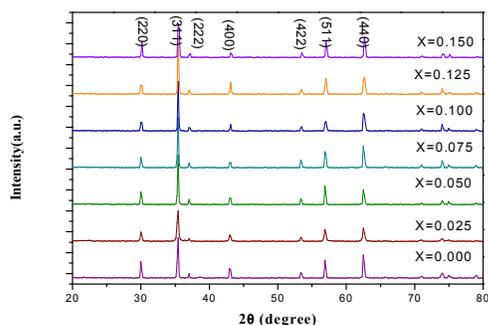


Fig. 1 X-ray diffraction patterns of $\text{Ni}_{0.4}\text{Cu}_{0.2}\text{Zn}_{0.4}\text{Cr}_x\text{Fe}_{2-x}\text{O}_4$

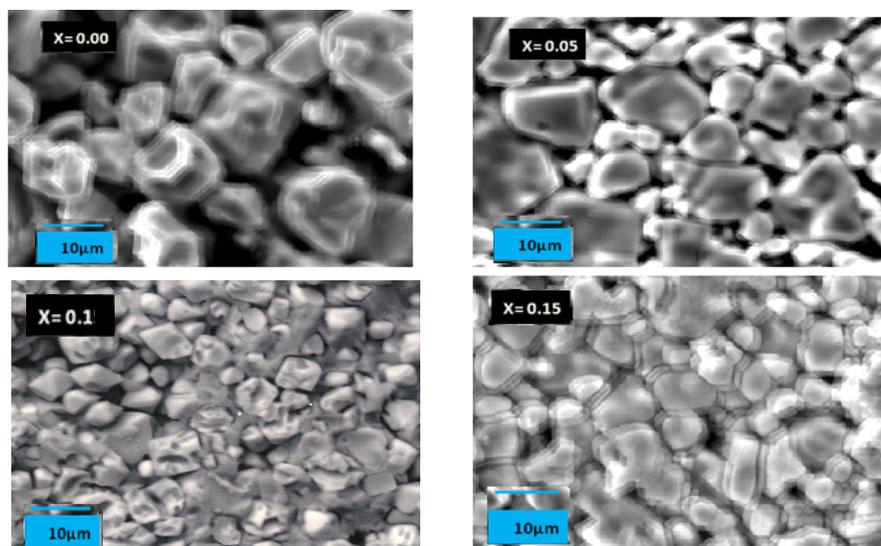


Fig. 3 SEM micrographs of $\text{Ni}_{0.4}\text{Cu}_{0.2}\text{Zn}_{0.4}\text{Cr}_x\text{Fe}_{2-x}\text{O}_4$ with $x = 0.0, 0.05, 0.1$ and 0.15 .

parameter fig.2 leads to increase of A-B interaction and hence T_c has to increase. Whereas, the number of magnetic ions presents in the two sub-lattices, as Fe^{3+} ions are gradually decreased due to Cr replacement which weakens the strength of A-B interactions causing decrease in T_c . This means that the effect of decreasing the number of magnetic ions overcomes the lattice parameter decrease.

3.4 Electrical Resistivity:

The dependence of dc electrical resistivity (ρ) at room temperature on Cr-concentration is shown in Fig. 8. The dc resistivity heightens with the raise in Cr-concentration. This behavior could be understandable as the chromium ions do not participate in the conduction process but limit the hopping probability between Fe^{2+} and Fe^{3+} ions [38]. Also, as grain size decreases, with increasing Cr-concentration, the number of grain boundaries increase and hence the resistivity enhanced.

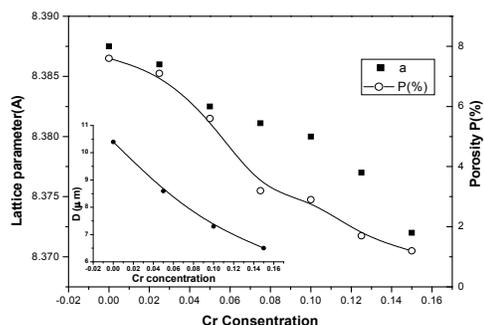


Fig. 2 Variation of lattice parameter a (\AA), Porosity, and average grain diameter (inset) with Cr-concentration

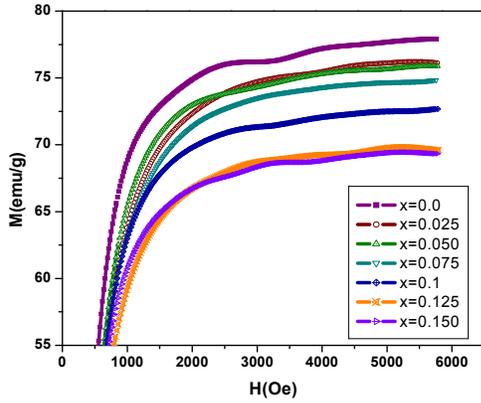


Fig. 4 Variation of magnetization M (emu/g) with H (Oe) of at room temperature.

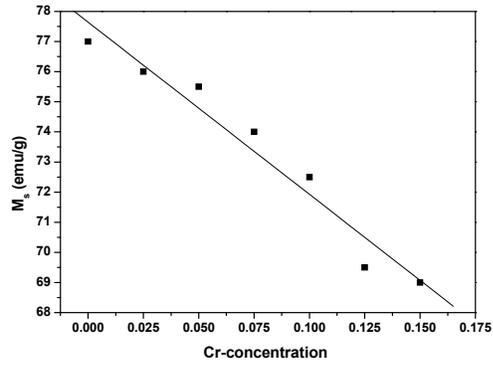


Fig. 5 Variation of saturation magnetization Ms (emu/g) with Cr-concentration.

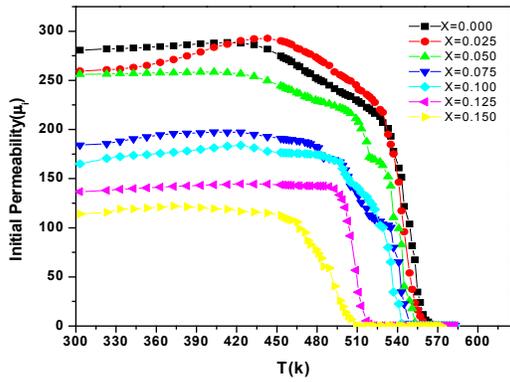


Fig. 6 Variation of initial permeability (μi) with temperature

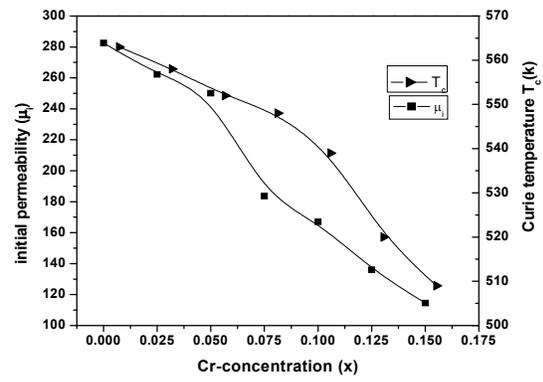


Fig. 7 Variation of initial permeability (μi) at room temperature and Curie temperature (Tc) with Cr-concentration.

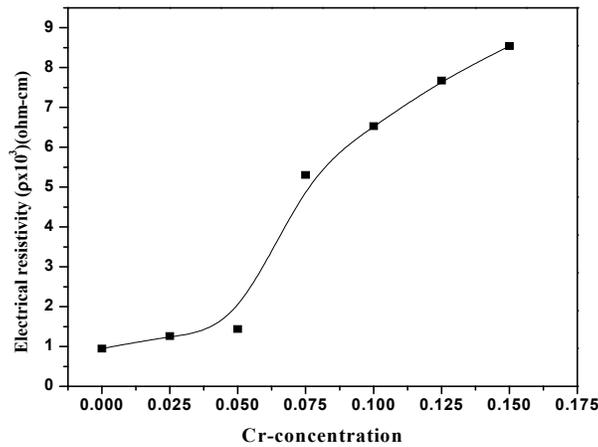


Fig.(8). The dependence of the electrical resistivity (ρ) at room temperature On Cr-concentration

4-Conclusion:

The effect of Cr-ion substitution on structure, magnetic and electrical properties of NiCuZn ferrites had been investigated. The results demonstrate decay in magnetic properties and enhancement in the electrical properties where, lattice parameter, porosity decreased with Cr³⁺-ion substitution. The saturation magnetization, the initial permeability, Curie temperature reduced with increasing Cr-concentration, but dc resistivity improved.

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