

Effect of SiO₂ addition on the electrical properties of Ni-doped Cu-Cr ferrites

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Abstract: Ferrite samples having the composition (Cu_{1-x}Ni_xCr FeO₄; x = 0.2, 0.4, 0.6 and 0.8) was prepared using the usual ceramic technique. Then composites of these ferrites with SiO₂ were prepared by mixing 25% weight of SiO₂ powder with 75% weight of each composition of the ferrite powders. The dc conductivity and the dielectric properties of the samples were investigated. The dielectric constant (ϵ') and ac conductivity (σ'_{ac}) were measured at different frequencies and temperatures. The variation of the ac conductivity with temperature shows semiconducting behavior, whilst with frequency it shows almost constant values over a wide range especially at high temperatures and a slight increase with increasing frequency at lower temperatures. This behavior indicates that the studied composites may be good candidates for many applications. The dielectric constant shows some broad peaks which shifts to higher frequencies with increasing the temperature. These results are explained as due to the existence of two types of charge carriers (n and P) in Cu containing ferrites. The algebraic sum of their contribution to the polarization gives rise to those peaks. The results show that adding silicon dioxide has reduced the conductivity significantly or in other words increased the resistivity of the material, which improves the dielectric properties of the system to be used in applications that requires very low levels of eddy currents.

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Key words: Dielectric Properties; DC Conductivity; Soft Ferrites.

1. Introduction

Ferrites are one of the most versatile magnetic materials for daily use. They have many applications in both low-and high –frequency devices such as microwave devices, power transformers in electronics, rod antennas and read-write heads for high speed digital tapes. Mixed copper ferrites, in particular, have been commercially used for many years in these applications [1,2]. It is important to investigate how compositional modifications in the material can contribute to improve both the magnetic and electrical properties. To reduce eddy current losses, one uses special additions , for example, CaO or SiO₂, which ensure the electric and magnetic isolation of individual grains (crystallites). Many researchers have been active in preparing systems in which magnetic crystalline particles/ grains are separated by means of a nonmagnetic material in order to improve both magnetic and electrical properties. Of these nonmagnetic materials (e.g., Al₂O₃, Ti O₂, Si O₂, etc.) ,SiO₂ was observed to serve the purpose more favorably than its counterparts [3]. The present work is devoted to investigate the effect of adding 25% weight of SiO₂ to four samples of the composition (Cu_{1-x}Ni_xCr FeO₄; x = 0.2, 0.4, 0.6 and 0.8) on some of their electrical properties.

2-Experiment

Four samples of the composition (Cu_{1-x}Ni_xCr FeO₄; x = 0.2, 0.4, 0.6 and 0.8) previously prepared by the conventional ceramic method are used in the

present investigation; the details of preparation and characterization had been reported in a previous work [4]. The X-ray diffraction patterns ensured the formation of the required system and the IR and Mössbauer spectroscopy analysis of the samples had been published too in the same reference [4] . In the present work, the above compositions were mixed with 25% weight of SiO₂, and pressed to disc-shaped pellets then sintered at 1000°C. For the measurements of ac conductivity (σ'_{ac}), dielectric constant (ϵ') and dielectric loss ($\tan\delta$), the surfaces of the disc-shaped pellets were coated with a thin layer of silver paste to provide good contact with the external electrodes. The measurements were carried out inside an evacuated silica tube by using a complex impedance technique [5,6]. In this technique an ac voltage V with frequency f is applied to the sample. A small resistor R is connected in series with the sample. The current is given by ($I = V_R/R$) where V_R is the drop voltage on R. A lock-in amplifier (SR 510 Lock-In Amplifier Stanford Research Systems) is used in the circuit to measure the voltage V_R , the frequency f of the applied voltage and the phase difference (ϕ) between V and V_R simultaneously. From these readings, the ac conductivity σ'_{ac} , the dielectric constant (ϵ') , and the dielectric loss ($\tan\delta$) can be calculated.

3. Results and discussion

3.1. The dielectric constant behavior

Fig. 1 (a-d) shows the variation of the dielectric constant ϵ' with the applied frequency in logarithmic scale for the four investigated compositions ($\text{Cu}_{1-x}\text{Ni}_x\text{Cr FeO}_4$; $x=0.2, 0.4, 0.6, 0.8$) respectively. It can be seen obviously two types of behavior; the first, observed at low temperatures, is a traditional dispersion or decrease of the dielectric constant with increasing frequency, and this behavior is always attributed to the lagging of the hopping charge carriers -between Fe^{2+} and Fe^{3+} ions at localised sites- responsible for polarization behind the applied field as the frequency increases [6,7]. The second behavior was observed at relatively high temperatures, where the dielectric constant at first, increases with increasing frequency until reaching a peak after which it displays the traditional relaxation, this behavior can be explained on the basis of Rezlescu and Rezlescu assumption [8]; where this behavior was attributed to a collective contribution of electrons and holes to the polarization. Moreover, the peak appearing in the dielectric constant versus frequency curve, shifts towards higher frequencies with increasing temperature, and this is due to the increase of the thermally activated hopping frequency of the charge carriers between localized sites. From the same figures, we can see that, generally the dielectric constant values are high particularly at low frequencies, this can be attributed to the interfacial polarization known to occur in heterogeneous structures [7].

3.2. The dielectric loss behavior

The variation of the dielectric loss factor ($\tan\delta$) with frequency in logarithmic scale ($\log f$) for the compositions ($\text{Cu}_{1-x}\text{Ni}_x\text{Cr FeO}_4$; $x=0.2, 0.4, 0.6$ and 0.8) is shown in Fig.2(a-d). All of the compositions show an exponential decrease in the dielectric loss tangent with increasing frequency. The dielectric loss factor decreases rapidly at low frequency region, while the rate of decrease is slower in the high frequency region and becoming almost frequency and temperature independent at the end of the investigated range. The loss tangent ($\tan\delta$) is defined as the ratio of the loss or resistive current to the charging current in the sample. Also, it is known that, there is a strong correlation between the conduction mechanism and the dielectric constant behavior (the polarization mechanism) in ferrites. From these two considerations we can see that the behavior of $\tan\delta$ with frequency is showing the expected decrease with increasing frequency. Also, the increase in $\tan\delta$ value (i.e. in loss current) with increasing temperature ensures the semiconducting nature or the thermally activated mechanism of conduction in the samples[9]. Moreover, such a behavior may also be explained on the basis that in low frequency region, which

corresponds to high resistivity (due to the grain boundary), more energy is required for electron exchange between Fe^{2+} - Fe^{3+} pairs in the octahedral sites, as a result the loss is high. Moreover this is in consistency with the mathematical definition of $\tan\delta$ mentioned above which is equal to ϵ''/ϵ' ; where ϵ'' represents a measure of the resistive current and ϵ' represents a measure of the capacitive current in the electrical equivalent circuit of the sample. In high frequency region, which corresponds to low resistivity (due to grains), a small energy is required for electron transfer between Fe ion pairs at the octahedral site [10].

3.3. The ac conductivity behavior

Fig.3 (a-d) illustrates the frequency dependence (in logarithmic scale) of the ac conductivity σ_{ac} for the four investigated compositions at different values of temperature. By checking out Fig.3 carefully, we can find that the conductivity is almost constant in a wide range of frequency in the temperature range $> 400\text{K}$. This indicates that the capacitive part in the samples' electrical equivalent circuit is not as much significant as the resistive part [6]. From Fig.3 (a-d) also we can see that the variation with temperature is more noticeable, where we can see that the general behavior of all samples is similar to semiconductors i.e. as the temperature increases, the resistivity of the samples decreases [11], this is in agreement with the well established information that spinel ferrites can be categorized as semiconductors [12]. Normally, conduction in ferrites depends on the combined influence of several factors such as Fe^{2+} ion concentration, grain size and microstructural homogeneity. The conduction mechanism involves electronic hopping between ion pairs of the same type of element on equivalent sub-lattice sites but having different valence state [7]. The probability of hopping depends upon the separation between ions involved in conduction process and activation energy [13]. In spinel ferrites, the distance between the cations in A-sites is more than the distance between cations in B-sites. Also, the degree of covalency for the A-site cations is known to be higher than that of the B-site cations [14]. Due to this information, the mobility of electrons and holes in the A-sites is expected to be smaller than that in the B-sites. The MÖssbauer studies previously performed for these compositions [4] clearly show that the Fe^{3+} ion concentration decreased in B-site due to Ni-Cr-Cu substitution. The resistivity of the spinel ferrites is controlled by $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio on the B-sites. Substitution of other ions for Fe^{3+} at B-sites decreases the number of Fe ions contributing to hopping process, which in turn leads to the increase in the resistivity. Cr ions do not

participate in the conduction process and also limit the degree of $\text{Fe}^{2+}\text{-Fe}^{3+}$ conduction by blocking up the $\text{Fe}^{2+}\text{-Fe}^{3+}$ transformation, this effect as well as adding of SiO_2 leads to the same result. Furthermore, Cr^{3+} ions occupy the interstitial B-sites and result in distortion of lattice, creating internal stress, which confined the electron hopping and then reduce the Fe^{2+} ion generation [15]. Therefore, it is expected that the resistivity should increase upon doping, as observed. Increase in resistivity would also indicate decrease in eddy current losses as we can observe from the values of $(\tan\delta)$.

3.4. Composition dependence

Fig.4 (a-c) displays the Ni content dependence of the dielectric constant (ϵ'), the dielectric loss ($\tan\delta$) and the ac conductivity σ'_{ac} , respectively at three selected temperatures ($T=308\text{K}$, 363K , 463K). It can be observed that ϵ' , σ'_{ac} and $\tan\delta$ values follow the same trend with increasing the Ni ion content. At first they decrease with increasing Ni, which is expected as the Cu content decreases. With further increase in Ni ion content a slight increase in these three variables occurs, which may be explained as due to the contribution of Ni ions to the conduction and polarization processes as the Ni content increases, since it is well known that the conduction in Ni containing ferrites by hopping mechanism taking place between divalent and trivalent ions of Ni as well as those of Fe on (B-sites), this may be expressed as follows: $\text{Fe}^{2+}\text{-Fe}^{3+} + e^-$ or $\text{Ni}^{3+}\text{-Ni}^{2+} + e^+$ [16]. Moreover, this similarity in the behavior of conductivity and dielectric constant ensures the well known assumption that they both have the same mechanism in ferrites [7].

3.5. The dc conductivity behavior

Fig. 5 illustrates the variation of the dc electrical conductivity ($\ln \sigma_{dc}$) with temperature ($10^3/T$) for the studied samples. It is obviously shown that the dc conductivity exhibits a semiconducting behavior where it increases with increasing the temperature following the Arrhenius relation

$\sigma = \sigma_0 e^{-E_g/kT}$, where E_g is the activation energy for conduction, k is Boltzmann constant, and T is the absolute temperature. By careful investigation of the figure, there are two distinct regions with different slopes for each sample characterized by a certain transition temperature, T_C . Each region is characterized by a certain activation energy, E_1 for the low temperature region and E_2 for the high temperature region. The transition temperatures, T_C and the activation energies, E_1 and E_2 for all samples are calculated and given in Table 1. Since it is known theoretically that on passing

through the Curie point a change must occur in the gradient of the straight lines of $\ln \sigma_{dc}$ vs. $1/T$ [17] due to the change in the exchange interaction between A and B sites near the Curie point, the transition temperature T_C is often ascribed to the magnetic transition from the ferrimagnetic state to the paramagnetic state. Comparing the values of T_C of the investigated samples with the Curie points reported in many references [18-21] for almost similar compositions, one can find that the calculated T_C 's values in the present work are in good agreement with them. Therefore, this ensures that these transition points are due to the magnetic transition from ferrimagnetic state to paramagnetic state.

It is apparent that the activation energies in the paramagnetic region are higher than those in the ferrimagnetic region. This finding can be attributed to the disordered states of the paramagnetic region and the ordered states of the ferrimagnetic region. This result also suggests that the conduction process is affected by the change in magnetic ordering. As mentioned above the electrical conduction in ferrites can be explained by the Verwey model of electron hopping which involves the exchange of electron between ions of the same element present in different valance states, and distributed randomly over crystallographically equivalent lattice sites. The increase in Ni substitution ions at B-site leads to replacement of Fe^{3+} ions at the B site which leads consequently to a decrease of ferrous ions formed.

Moreover, It is worth mentioning that before adding 25% weight of SiO_2 to the samples the dc conductivity of these compositions at room temperature had values of a relatively bad dielectric ranging from $1.6 \times 10^{-3} (\Omega^{-1}\text{cm}^{-1})$ and $1.6 \times 10^{-5} (\Omega^{-1}\text{cm}^{-1})$, while after adding the SiO_2 the measured values of dc conductivity for the same compositions at room temperature ranges from 6.8×10^{-8} for the composition of ($x=0.4$) and 3.9×10^{-7} for the composition with ($x=0.2$) as it can be seen from Fig.5.

From a practical point of view, as the dc conductivity decreases significantly the eddy current will be reduced improving the performance of these materials as good dielectrics having useful magnetic properties.

4. Conclusion

The abnormal behavior of the dielectric constant as a function of frequency at relatively high temperatures results from a collective contribution to the polarization process from two types of charge carriers (n and p) expected in Ni and Cu containing ferrites.

Adding SiO_2 to the ferrite samples has greatly improved the dielectric character of the

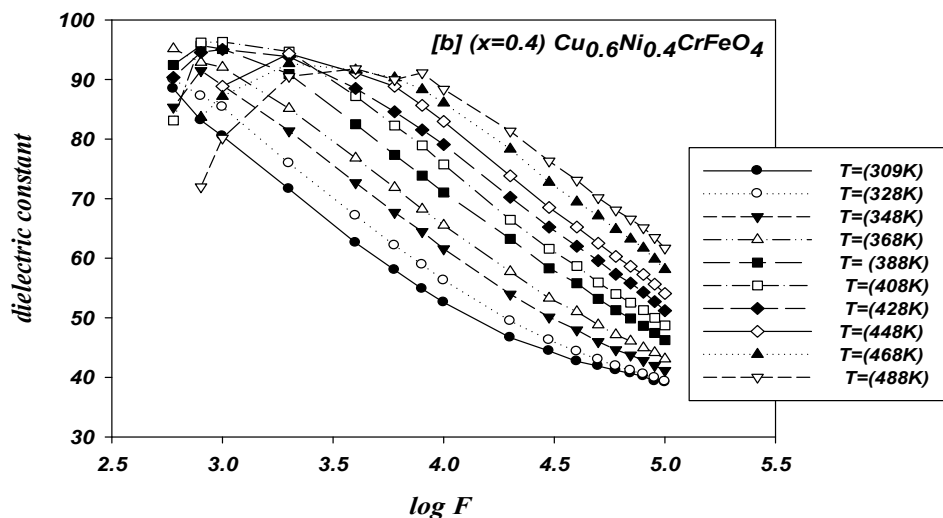
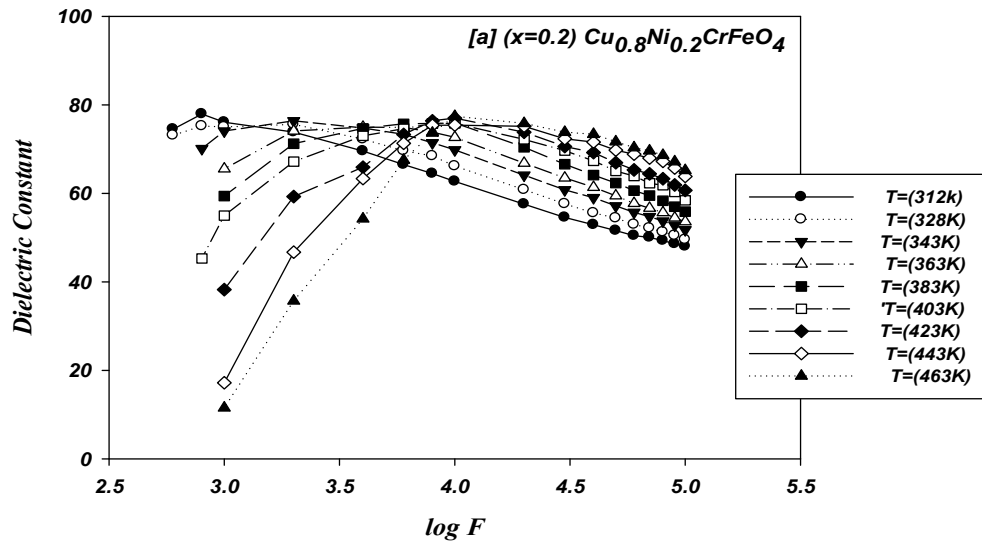
materials which may be very useful in applications that require the reduction of eddy currents.

seems to be the best one for the above mentioned applications.

By comparing the results of different samples, the composite ($\text{Cu}_{0.6}\text{Ni}_{0.4}\text{CrFeO}_4/\text{SiO}_2$)

Table (1): Ni content x dependence of activation energies and transition temperature for all the samples ($\text{Cu}_{1-x}\text{Ni}_x\text{CrFeO}_4/\text{SiO}_2$); x = 0.2, 0.4, 0.6 and 0.8

Ni content(x)	E_p (ev)	E_f (ev)	T_c (K)
0.2	0.27	0.18	383
0.4	0.349	0.221	392
0.6	0.284	0.204	403
0.8	0.303	0.216	421



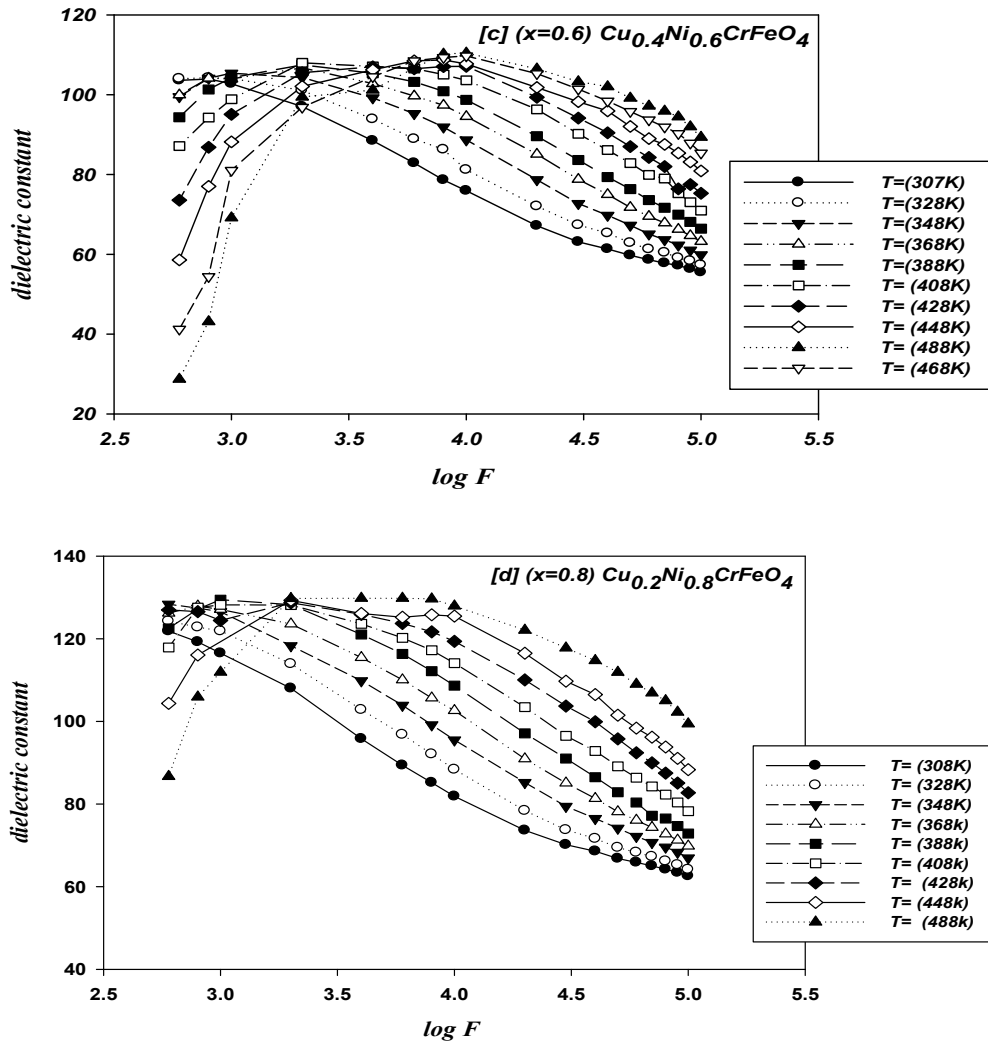
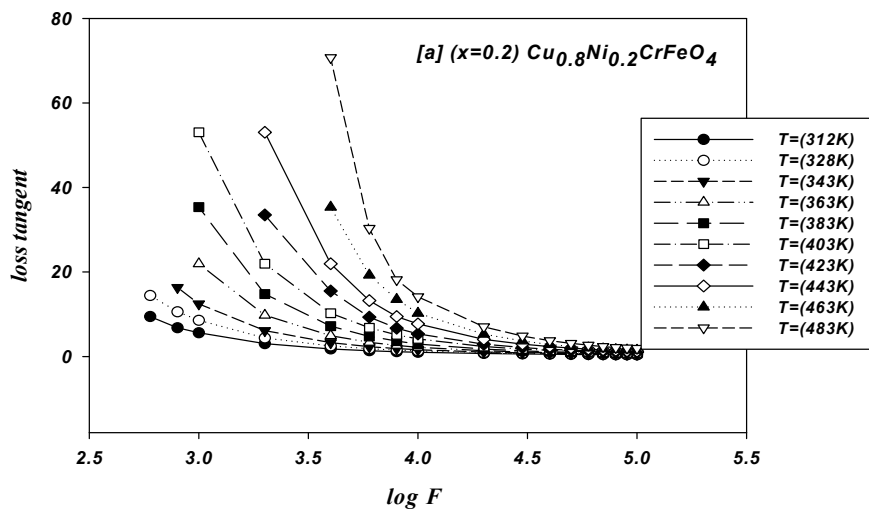


Fig. (1) Frequency dependence of dielectric constant for all the samples ($\text{Cu}_{1-x}\text{Ni}_x\text{CrFeO}_4/\text{SiO}_2$); (a) $x = 0.2$, (b) $x = 0.4$, (c) $x = 0.6$ and (d) $x = 0.8$



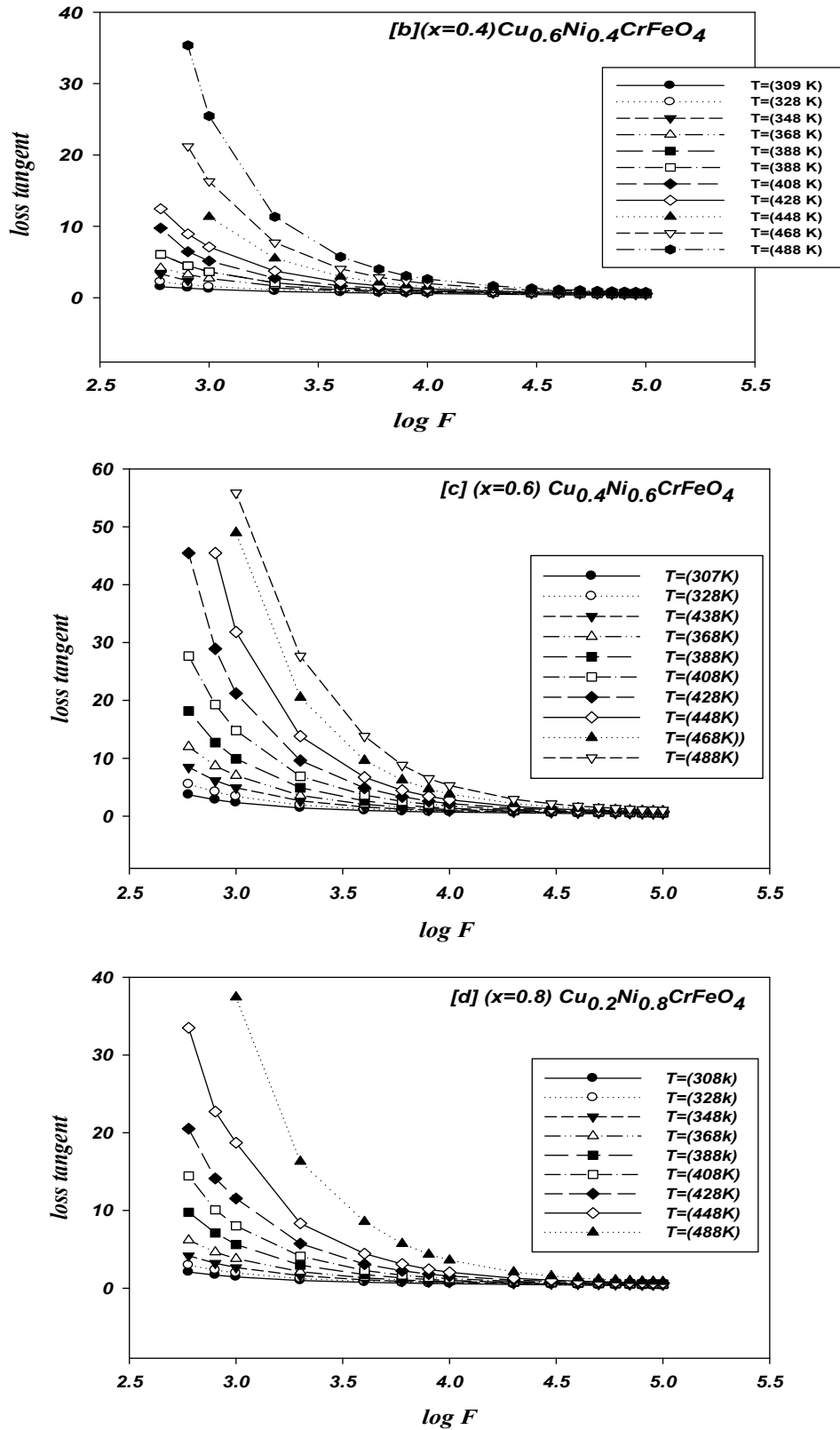
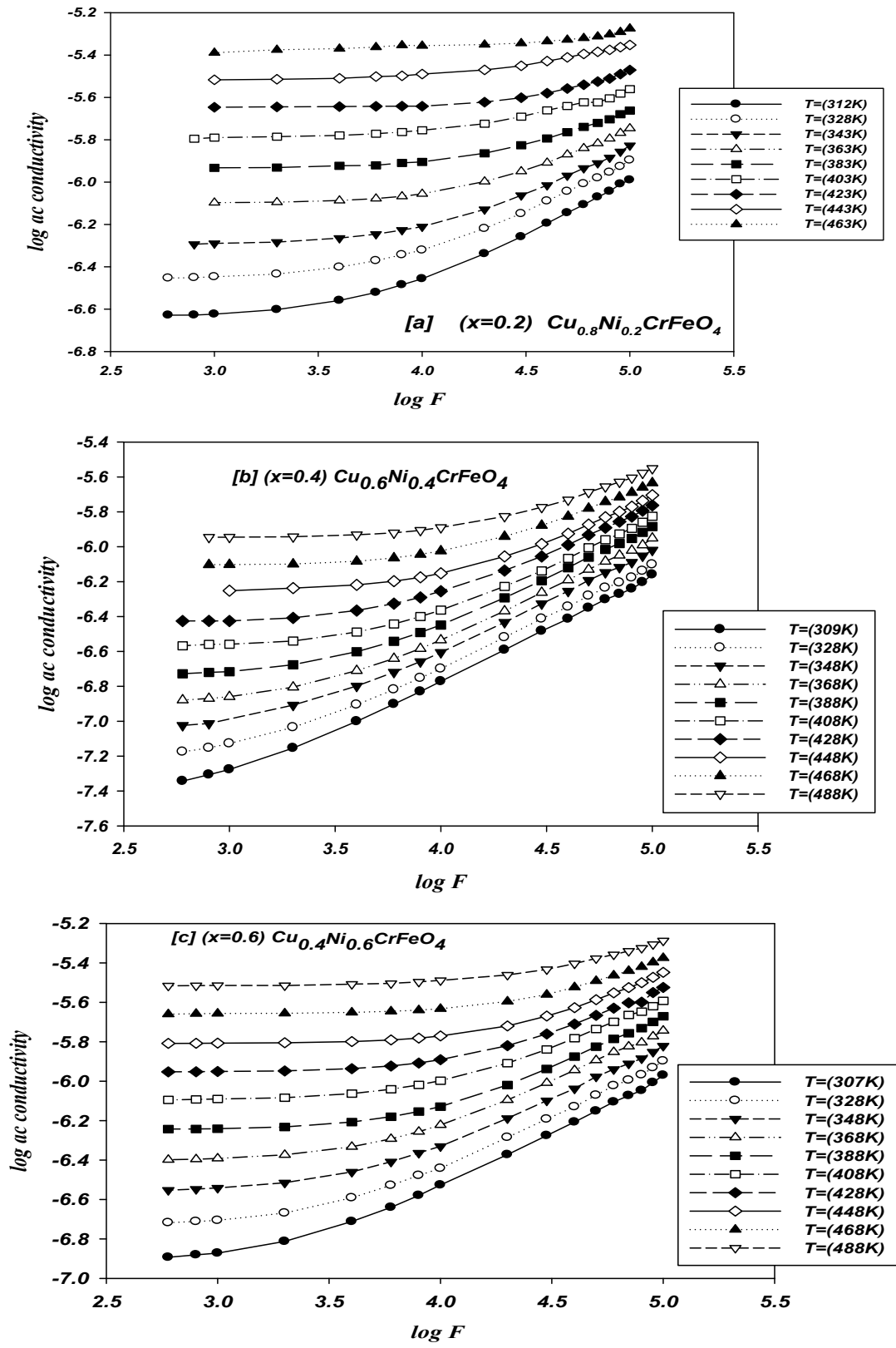


Fig. (2) Frequency dependence of loss tangent for all the samples ($\text{Cu}_{1-x}\text{Ni}_x\text{CrFeO}_4/\text{SiO}_2$); (a) $x = 0.2$, (b) $x = 0.4$, (c) $x = 0.6$ and (d) $x = 0.8$



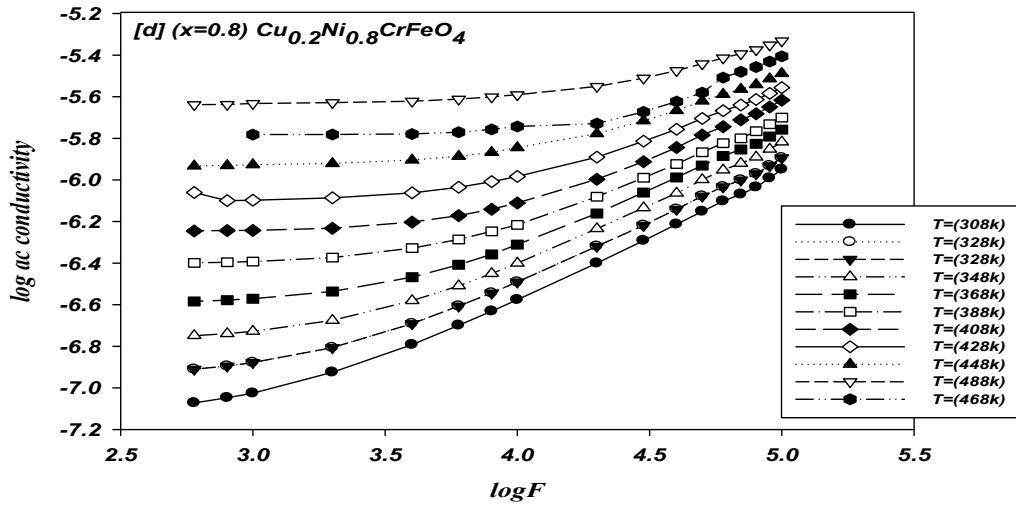


Fig. (3) Frequency dependence of ac conductivity for all the samples ($Cu_{1-x}Ni_xCr FeO_4/SiO_2$); (a) $x = 0.2$, (b) $x = 0.4$, (c) $x = 0.6$ and (d) $x = 0.8$

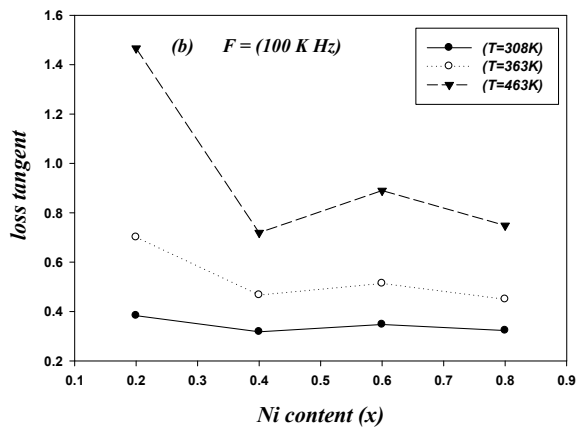
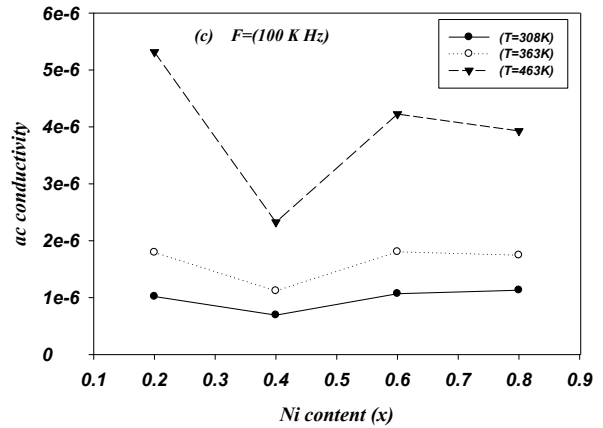
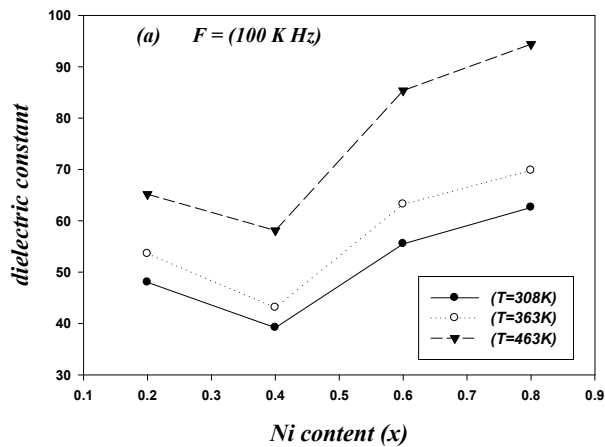


Fig. (4) Ni content x dependence of (a) dielectric constant, (b) loss tangent and (c) ac conductivity for all the samples ($Cu_{1-x}Ni_xCr FeO_4/SiO_2$); $x = 0.2, 0.4, 0.6$ and 0.8

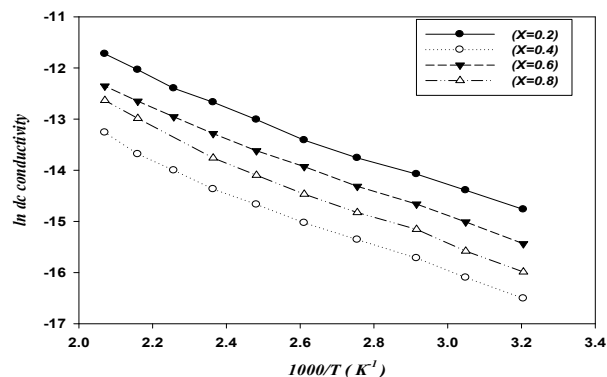


Fig. (5) 1000/T dependence of ln dc conductivity for all the samples ($\text{Cu}_{1-x}\text{Ni}_x\text{Cr FeO}_4/\text{SiO}_2$); $x = 0.2, 0.4, 0.6$ and 0.8

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