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Study of the dielectric behavior of Co–Ni–Li nanoferrites

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ABSTRACT

The ac conductivity and dielectric properties of $Co_{0.5}Ni_{0.5-2x}Li_xFe_{2+x}O_4$ nanoparticle ferrite samples (from $x=0.00$ to 0.25 in step of 0.05) synthesized by the citrate precursor method were studied by using a complex impedance technique. The effect of varying the frequency, temperature and composition on ac conductivity, dielectric constant and dielectric losses was discussed and justified in terms of hopping of charge carriers between Fe^{+3} and Fe^{+2} ions, Ni^{+2} and Ni^{+3} ions and Co^{+2} and Co^{+3} ions. The obtained results of the variation of S parameter with temperature show that the classical barrier hopping model is the most probable mechanism in the samples under investigation. While the results of the Cole–Cole diagrams of M'' vs. M' at different temperatures ensure the presence of grain and grain boundaries having different but comparable conductivities in the investigated nanoparticle samples and also indicate that the studied ferrites exhibit the so called "electric stiffness".

1. Introduction

Investigation of the nanosized spinel ferrites is one of the most vital and fast growing areas of research in the field of nanotechnology. The excellent electrical and magnetic properties of nanoferrites make them suitable for high frequency applications in the field of telecommunication [1,2]. In early days, garnets were used for microwave devices where they had high resistivity and low dielectric losses. But, because of low Curie temperature, high stress sensitivity and high cost of garnets, the focus was directed towards lithium ferrites [3,4]. Lithium based ferrites have become important materials for microwave applications such as in circulators, isolators, phase shifters, etc. due to their high resistivity, low dielectric losses, high Curie temperature, squareness of hysteresis loop and low costs [5–9]. Electrical conductivity, which gives valuable information about conduction mechanism, is one of the important properties of ferrites. It depends on the method of preparation, types of additives, sintering time and temperature [4,10]. Moreover, electrical conductivity has a significant effect on the dielectric polarization in the spinel ferrites. Many researchers have studied the dielectric properties of Li substituted spinel ferrites such as Li–Ni–Cu [1], Li–Ni–Mg [11], Li–Mg–Zn [12], Li–Co–Zn [13], Li–Ni–Zn [14], Li–Ga [15,16], and Li–Cr [17,18]. However, no other author had investigated Li substituted Co–Ni ferrites but since an improvement has been observed by the authors in the magnetic properties of Co–Ni ferrites by doping Li ions [19], therefore, the aim of the present work is to study the effect of adding the Li ions to the nanosamples on their dielectric behavior too.

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2. Experimental

Nanoparticles of $Co_{0.5}Ni_{0.5-2x}Li_xFe_{2+x}O_4$ with x ranges from 0.00 to 0.25 in steps of 0.05 were prepared by using the citrate precursor method. The details of preparation and characterization by X-ray diffraction, particle size analysis and TEM imaging, IR spectroscopy, and VSM measurements have been reported as mentioned earlier in a previous publication [19]. The powders of different compositions were pressed into disc-shaped pellets by applying a pressure of about $2.6\times10^8\ N/m^2$ in order to prepare them for the dielectric measurements which have been performed by using a complex impedance technique (Lock-in amplifier Stanford SR 510 type). The surfaces of each disc-shaped sample have been coated with silver paste to improve the contact with the electrodes inside an evacuated silica tube cell surrounded by a home-made heater. The block diagram of the circuit used for the ac electrical measurements is illustrated in reference [20]. Moreover, the details of the equations used in calculating the ac conductivity, the dielectric constant, and the loss tangent $\tan\delta$ as functions of frequency at different temperatures were reported earlier [14].

3. Results and discussion

3.1. Frequency dependence

In general, it is known that the total conductivity σ'_{ac} at a given angular frequency ω consists of two components [14].

$$\sigma'_{ac}=\sigma_0(T)+\sigma(T,\omega) \tag{1}$$

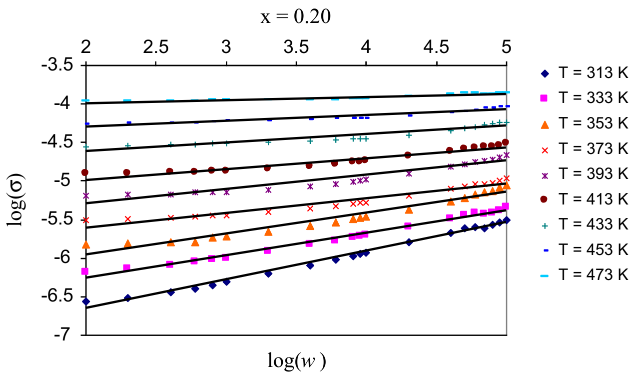

Fig. 1. The frequency dependence of $\sigma(\omega)$for the sample $x=0.20$ at various temperatures.

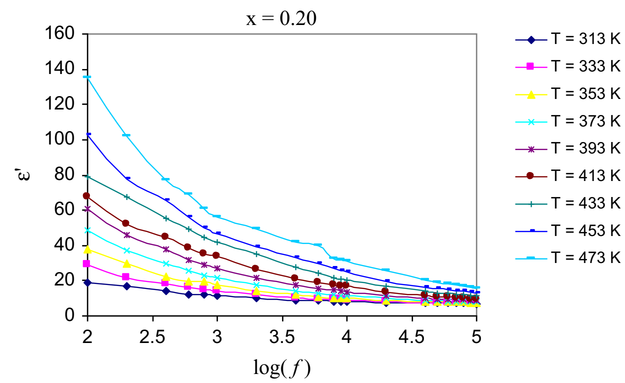

Fig. 2. The frequency dependence of the dielectric constant ε' for the sample $x=0.20$ at various temperatures.

The first term $\sigma_0(T)$ is actually the dc electrical conductivity$\sigma_{dc}(T)$; it is temperature dependent and frequency independent. It is related to the drift mobility of electric charge carriers. The second term $\sigma(T,\omega)$ is frequency and temperature dependent; it is attributed to the dielectric relaxation caused by the localized electric charge carriers and obeys the power law form [16]:

$$\sigma(T,\omega)=A\omega^S \tag{2}$$

where A and S are temperature dependent parameters. It was reported that the exponent parameter S can have values between 0 and 1 [16]. The frequency dependence of the ac electrical conductivity in logarithmic scale $\log\sigma(\omega)$, real dielectric constant ε' and dielectric loss tangent $\tan\delta$ of the sample $x=0.20$ at selected temperatures are shown in Figs. 1, 2 and 3, respectively. As can be seen from the figures, $\log\sigma(\omega)$ increases while ε' and $\tan\delta$ decrease as the frequency increases. The same behavior has been seen in other samples. This behavior of the spinel nanoferrite samples is attributed to the Maxwell–Wagner [21] interfacial polarization in accordance with Koop's phenomenological theory [22] which describes the ac electrical conductivity in the heterogeneous structure of ferrites, where they are made up of well conducting regions (grains) separated by poor conducting layers (grain boundaries). In this case, the ac conduction takes place by the hopping mechanism through the interaction Fe^{3+}–O–Fe^{3+}, Ni^{2+}–O–Ni^{2+} and Co^{2+}–O–Co^{2+} over the octahedral B-sites. When charge carriers reach the grain boundary through hopping, they will pile up due to their higher resistivity producing interfacial polarization. These resistive grain boundaries were found to be more effective at lower frequencies while, the conductive ferrite grains are more effective at higher frequencies [23–25]. This explains the increase in $\sigma(\omega)$ as ω increases.

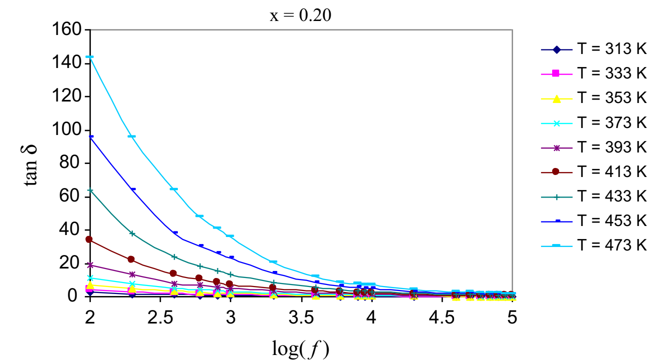

Fig. 3. The frequency dependence of the loss tangent $\tan\delta$ for the sample $x=0.20$ at various temperatures.

Also, it is well known from literature that, there is a strong correlation between the conduction mechanism and the dielectric behavior in ferrites [26], based on an assumption that the mechanism of polarization process in ferrites is similar to that of the conduction process [27]. Therefore, ε' decreases as the frequency of the applied field is increased as shown in Fig. 2 because the polarization cannot follow its alternations.

It is obviously seen in Fig. 3 that the loss tangent $\tan\delta$ decreases rapidly at low frequency than at high frequency. Such behavior may be explained as follows: at low frequency, where the resistive grain boundaries effect is predominant, more energy is required for the electron exchange in the interaction Fe^{3+}–O–Fe^{3+} and hole exchange in the interaction Ni^{2+}–O–Ni^{2+} and Co^{+2}–O–Co^{+2} at the octahedral sites and consequently the loss is high. Moreover, the dielectric loss tangent depends on other factors such as stoichiometry, Fe^{2+} content, and structure homogeneity which in turn depend upon the composition and sintering temperature of the samples [28]; all these factors may affect the value of the loss tangent such that the final net is as shown in Fig. 3.

3.2. Temperature dependence

The temperature dependence of the ac electrical conductivity σ'_{ac}, dielectric constant ε' and dielectric loss tangent $\tan\delta$ of the sample $x=0.20$ at selected frequencies is shown in Figs. 4, 5 and 6, respectively. It can be seen that σ'_{ac},ε', and $\tan\delta$ increase with increasing temperature ensuring the semiconducting behavior which characterizes ferrites as reported in literature [29]. All other samples show the same behavior. This can be interpreted as mentioned above in the light of the strong correlation between the conduction mechanism and the dielectric behavior in the spinel ferrites [26,30]. The increase in temperature thermally activates the charge carriers, increasing the charge carriers exchange interactions, thereby enhancing σ'_{ac}, ε', and $\tan\delta$.

3.3. Composition dependence

The composition dependence (Li content) of the ac conductivity σ'_{ac}, dielectric constant ε', and loss tangent $\tan\delta$ at 313 K and at 100 kHz is shown in Fig. 7(a), (b), and (c), respectively. It can be seen that, the ac conductivity σ'_{ac} decreases with increasing Li content except for an initial rise that has occurred from $x=0.0$ to $x=0.05$. This can be attributed to the effect of simultaneous contributions of different factors that depends on the composition such as grain size, density, porosity, and cation distribution. The initial increase of σ'_{ac} when the Li content increases from $x=0.0$ to 0.05 coincides with the increase of the grain size and measured density and the decrease of the porosity [19]. After then, the cation distribution becomes the predominant factor in decreasing the σ'_{ac}