

Dielectric Properties in Co-Ti Doped CaSrM Hexaferrites

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Abstract: The dependence of dielectric constant ϵ' and dielectric loss tangent $\tan \delta$ on frequency and composition have been investigated at fixed temperatures for polycrystalline $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Ti}_x\text{Fe}_{12-2x}\text{O}_{19}$ (where $0.0 \leq x \leq 0.8$) hexaferrites samples prepared by ceramic method. The measurements reveal that the samples under investigation have high values of ϵ' reached to 10^6 at 1 KHz and 600K. The experimental results indicated that ϵ' and $\tan \delta$ decrease as the frequency increases and temperature decreases. The studied samples showed an abnormal dielectric loss (or relaxation peaks) which were shifted towards higher frequency as the temperature increases. ϵ' and $\tan \delta$ increase as Co and Ti ions substitution increases up to $x \leq 0.4$, after that both parameters decreases. The activation energy for dielectric relaxation, E_D , was estimated for the samples. It is shown that, E_D , have low values (~ 0.08 - 0.18 eV) and have inverse proportional with the dielectric constant ϵ' .

Keywords – Dielectric properties, Doped M ferrite, Loss in ferrite, Dielectric relaxation, Activation energy.

I. Introduction

The hexagonal ferrites (M-type) have been attracted a considerable attention in technological and scientific research because of their high electrical resistivity, low eddy current, high Curie temperature, high stability and easy manufacturing. M hexaferrite is used as a basic material for permanent magnets, magnetic recording media, microwave and high frequency devices [1-3]. The polycrystalline ferrites are very good dielectric materials. During the process of preparation of ferrites in polycrystalline form, when the ferrite powder is sintered under slightly reducing conditions, the impurity ions such as Fe^{2+} were formed in the ferrite lead to high-conductivity grains. The grain boundaries are formed during the sintering process due to superficial reduction or oxidation of crystallites as a result of direct contact with the firing atmosphere [4]. Thus, the ferrite can be considered as high conductive grains separated by thin low conductive layers (grain boundaries) and behave as inhomogeneous dielectric materials. The AC electric field on the specimen is concentrated in the grain boundary regions. Therefore, dielectric properties are affected by grain boundary phase and the defect distribution in ferrites. However, the dielectric behavior is one of the most important properties of ferrites which very sensitive to the preparation conditions, such as; sintering time, sintering temperature and atmosphere, type and quantity of additives [5, 6]. The study of dielectric properties produces valuable information on the behavior of the localized electric charge carriers leading to greater understanding of the mechanism of dielectric polarization in these studied ferrite samples. The dielectric behavior of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Ti}_x\text{Fe}_{12-2x}\text{O}_{19}$ hexaferrite was not treated before in the literature. Therefore, the author aimed to study the effect of frequency, temperature and Co and Ti ions substitution on real dielectric constant and loss factor for the samples $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Ti}_x\text{Fe}_{12-2x}\text{O}_{19}$ ($0 \leq x \leq 0.8$).

II. Materials And Method

Polycrystalline samples CaSrCoTiM hexaferrites having the general formula $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Ti}_x\text{Fe}_{12-2x}\text{O}_{19}$ (where $x = 0.0, 0.2, 0.4, 0.6$ and 0.8) were prepared by a conventional double sintering ceramic method. The single phase M type hexagonal structure, lattice parameters, densities and porosity of these samples were checked by X-ray powder diffraction measurements. The details of the method of preparation and X-ray measurements were reported earlier [7]. The real dielectric constant ϵ' and loss tangent factor $\tan \delta$ of the samples were measured at room temperature in static air by the two probe method using an RLC bridge (model Hoki 3532-50 LCR HiTESTER). The values of loss tangent $\tan \delta$ and the capacitance of the sample (C) were recorded directly from the bridge. The dielectric constant, ϵ' , was calculated using the relation:

$$\epsilon' = Cd / \epsilon_0 A \quad (1)$$

where 'd' is the thickness of the sample, 'A' is the cross section area of the sample and ' ϵ_0 ' is the permittivity of free space ($\epsilon_0 = 8.854 \times 10^{-12}$ F.m⁻¹). This work was carried out at materials science laboratory, Physics Department, Faculty of Science, Kafrelsheikh University, Egypt.

III. Results And Discussion

3.1. Frequency dependence of dielectric constant ϵ' and loss tangent $\tan \delta$

The dielectric constant characterizes the most important electrical property of the dielectrics. The dielectric constant (or relative permittivity), ϵ^* of a dielectric material placed in the AC electric field is a complex quantity because the orientation polarization lags behind the polarizing electric field as the frequency of the applied field is increased. The complex dielectric constant, ϵ^* , can be expressed as:

$$\epsilon^* = \epsilon' + j\epsilon'' \quad (2)$$

where ϵ' is the real dielectric constant which characterizes the energy stored in the dielectric material, whereas the imaginary part ϵ'' represents the energy loss and $j = \sqrt{-1}$ the imaginary factor. The ratio between ϵ'' and ϵ' represents the loss tangent factor $\tan \delta$ ($\tan \delta = \epsilon''/\epsilon'$). Typical curves in Figure 1 shows the variation of the real dielectric constant ϵ' with the frequency of applied electric field (up to 1MHz) at constant temperatures for $x=0.2$. The samples with $0.2 \leq x \leq 0.6$ have high values of ϵ' in the order of magnitude of 2 - 6 at 1 KHz, whereas, samples with $x=0$ and 0.8 have low values of ϵ' ($\sim 10^1 - 10^3$ at 1KHz) These high values of ϵ' were observed for SrPbM hexaferrites [8], BaCoZn-W hexaferrites [9], Mg-Zn [4], Cu-Ge [10] and Li-Ni [11] spinel ferrites. Moreover, the dielectric constant decreases rapidly with the increasing in frequency and showing dispersion in the lower frequency region and attains a constant value beyond a certain frequency limit. The dispersion of dielectric constant at lower frequencies due to Maxwell Wagner [12, 13] type interracial polarization in agreement with the Koops phenomenological theory [14]. At lower frequencies the polarization in ferrite may be attributed to different types of polarization (electronic, atomic, interfacial and ionic, etc.). However, the high value and the dispersion in dielectric observed at lower frequencies are explained on the basis of space charge polarization due to inhomogeneities in dielectric materials. The inhomogeneities in ferrite, are impurities, porosity and grain structure and at higher frequencies it arises due to the contribution from electronic polarization [14]. Fig. 2 shows a typical variation of $\tan \delta$ with frequency for sample with $x=0.2$ at fixed temperatures. At lower frequencies, $\tan \delta$ is large and have a relaxation peaks moves toward high frequencies as temperature increases. The dielectric loss $\tan \delta$ decreases rapidly in the mid frequency region and in the high frequency region it becomes frequency independent. The loss factor shows a similar dispersion as that of dielectric constant with frequency. Such a behavior of $\tan \delta$ can be explained on the basis that in the mid frequency region, which corresponds to low conductivity of grain boundaries, more energy is required for the hopping of charge carriers, as a result the loss is higher. In the high frequency region, which corresponds to the high conductivity of grain, a small energy is required for transfer of charge carriers between octahedral sites. The relaxation peaks appear for all samples under investigation (except for $x=0.8$) at the low frequency region which means that the relaxation depend on the grain boundaries. The relaxation peak is observed when the hopping frequency of electric charge carrier is in resonance with the frequency of the electric field, i. e. maximum electric energy is transferred to the carriers and the loss increases rapidly at resonance [15]. The relaxation frequency f_{max} holds the relation $2\pi f_{max} \tau_D = 1$, where τ_D is the relaxation time for dielectric process. Using $\tan \delta(f)$ curves we were determined the values of f_{max} for all the samples which lies between 200- 700Hz. The linear relation between f_{max} and absolute temperature T is given by the Arrhenius relation $f_{max} = f_o \exp[-E_D/kT]$, where E_D is the activation energy for dielectric relaxation, f_o is a pre-exponential factor and k is the Boltzmann constant [16]. Using Arrhenius relation the activation energy E_D were estimated for the ferrite system. The values of dielectric relaxation activation energy E_D lies between 0.08 and 0.18 eV and in general have an inverse proportional to the values of dielectric constant ϵ' and loss factor $\tan \delta$.

3.2. Temperature dependence of dielectric constant ϵ' and loss tangent $\tan \delta$

The temperature dependence of ϵ' and $\tan \delta$ at selected frequencies are represented in Figs. 3 and 4, respectively. ϵ' and $\tan \delta$ increases as the temperature increases. The AC conduction in ferrite causes a local displacement of localized electric charge carriers in the direction of the external electric field, influencing dielectric polarization. As appointed out in recent work [7], the hopping electrons between Fe^{3+} and Fe^{2+} and transfer holes between Co^{2+} and Co^{3+} in the octahedral B-sites are responsible for electrical conduction in the

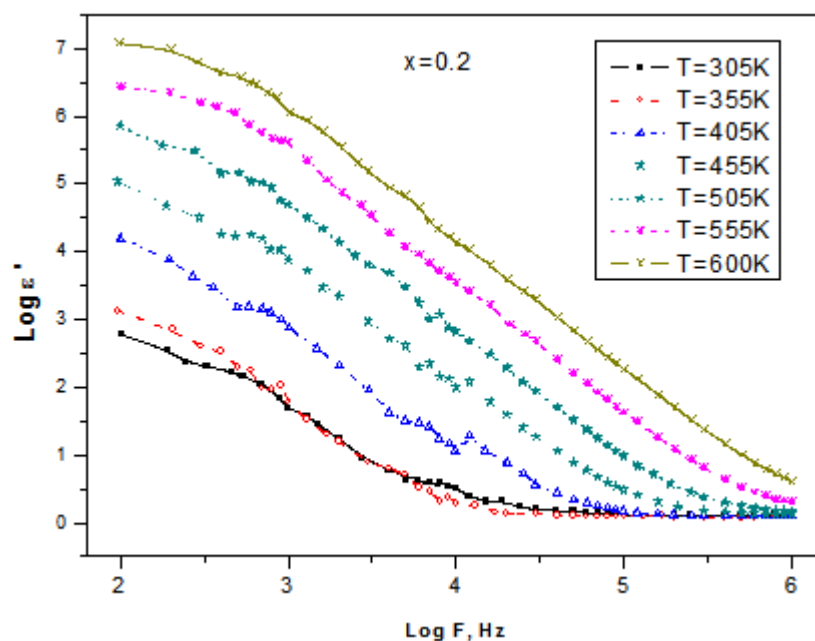


Figure 1: Typical frequency dependence of dielectric constant ϵ' for $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Ti}_{0.2}\text{Fe}_{11.6}\text{O}_{19}$ at selected temperatures.

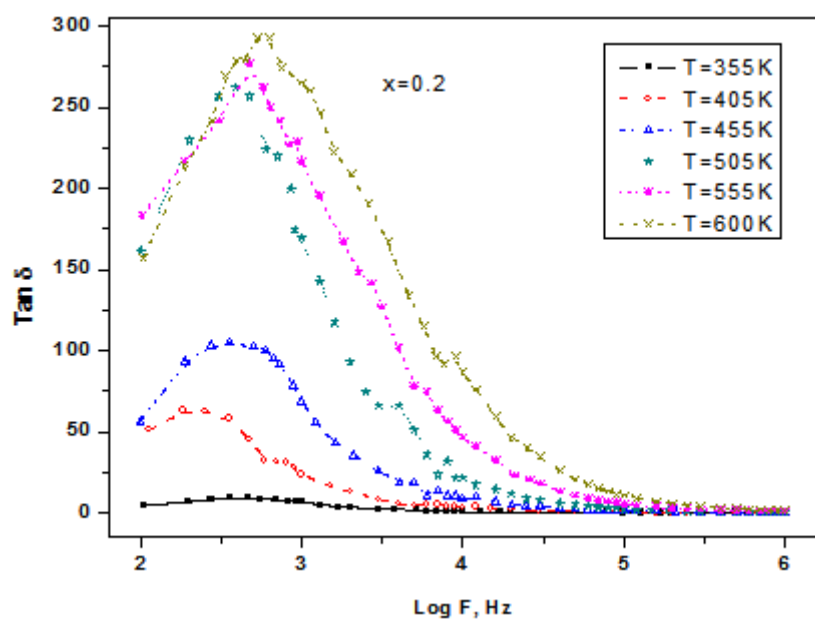


Figure 2: Typical frequency dependence of loss factor $\tan \delta$ for $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Ti}_{0.2}\text{Fe}_{11.6}\text{O}_{19}$ at selected temperatures.

samples. As the temperature increases, electrical conductivity increases due to the increase in thermally activated drift mobility of electric charge carriers according to the hopping process. Therefore, as the dielectric

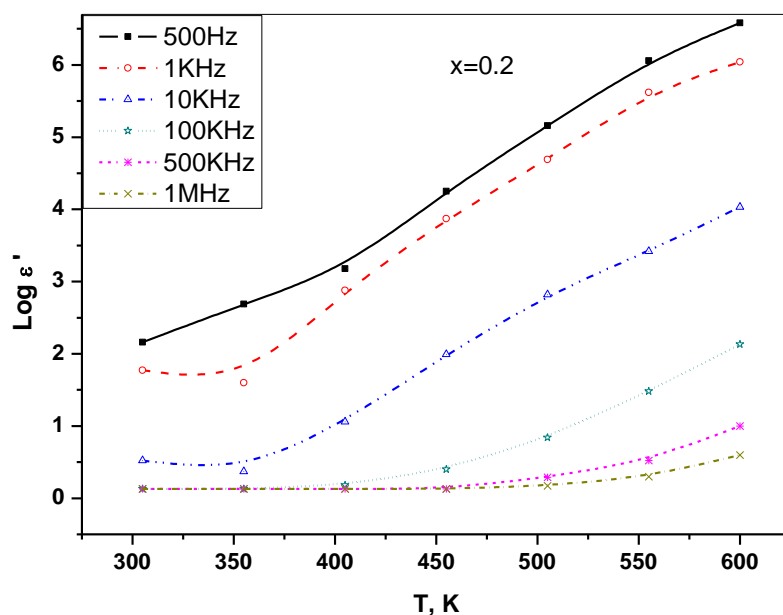


Figure 3: Temperature dependence of dielectric constant ϵ' for $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Ti}_{0.2}\text{Fe}_{11.6}\text{O}_{19}$ at selected frequencies.

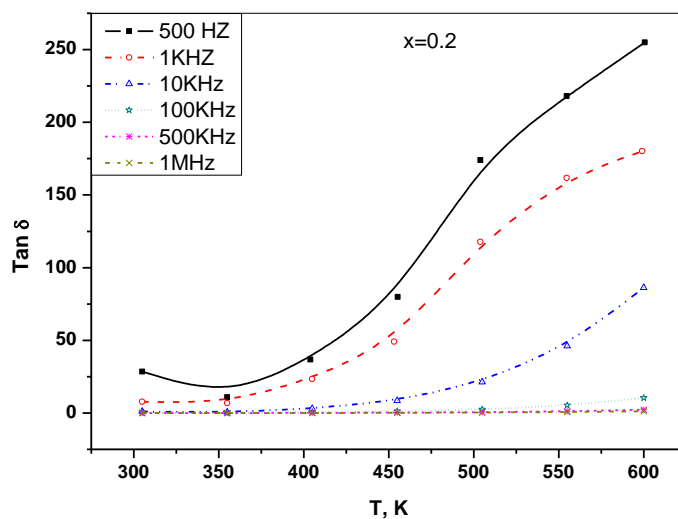


Figure 4: Temperature dependence of loss factor $\tan \delta$ for $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Ti}_{0.2}\text{Fe}_{11.6}\text{O}_{19}$ at selected frequencies.

polarization increases, causing a marked increase in dielectric constant and loss tangent as the temperature increases.

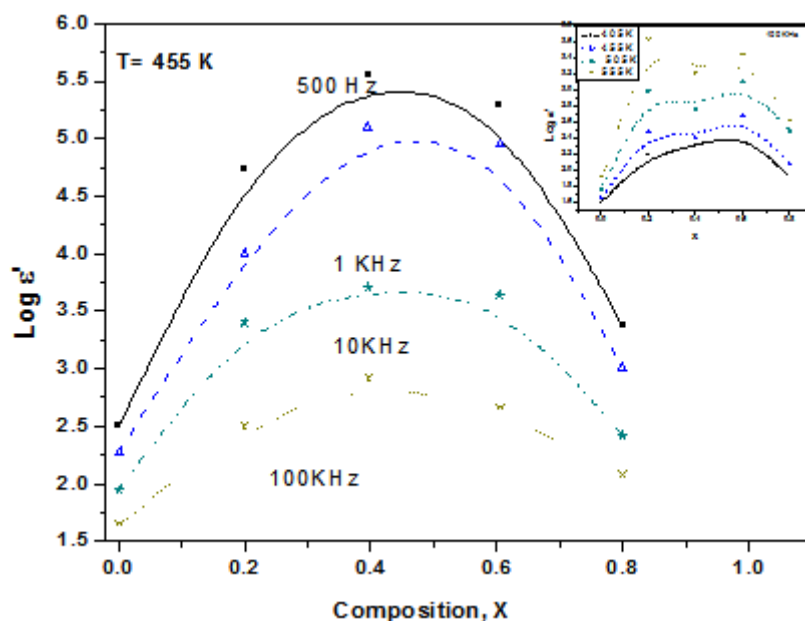


Figure 5: Compositional dependence of dielectric constant ϵ' at selected frequencies for the studied samples at 455K, the inset shows a typical $\epsilon'(x)$ plots at selected temperatures at 100KHz.

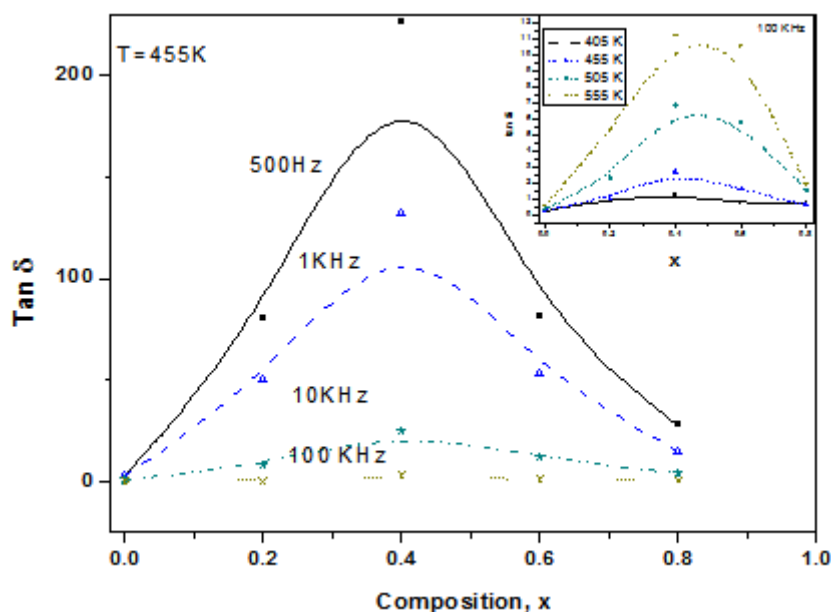


Figure 6: Compositional dependence of loss factor $\tan \delta$ at selected frequencies for the studied samples at 455K, the inset shows a typical $\tan \delta(x)$ plots at selected temperatures at 100KHz.

3.3. Composition dependence of dielectric constant ϵ' and loss tangent $\tan \delta$

The effects of replacing Fe^{3+} ions with Co^{2+} and Ti^{4+} ions on real dielectric constant ϵ' (as log scale) and dielectric loss factor $\tan \delta$ are illustrated in Figs. 5 and 6. ϵ' were drawn at selected frequencies of 0.5, 1, 10 and 100 KHz. Each of ϵ' and $\tan \delta$ increase with increasing the replacement of Fe^{3+} ions by Co^{2+} and Ti^{4+} ions to become maxima for $x = 0.4$ and started to decrease for $x > 0.4$. It was reported that the predominant conduction mechanism in such ferrite is due to hopping process of electrons between Fe^{2+} and Fe^{3+} and transfer holes between Co^{3+} and Co^{2+} ions. Fe^{2+} and Co^{3+} ions may be presented during the sintering process [17, 18]. The M-type ferrite crystallizes is a hexagonal structure with 64 ions per unit cell on 11 different symmetry sites. The 24 Fe atoms are distributed over five distinct sites; three octahedral (B) sites (12k, 2a, and $4f_2$), one tetrahedral (A) site ($4f_1$) and one a new type of interstitial (C) site (2b). The last one is not found in spinels and surrounded by five oxygen ions constituting a trigonal bi-pyramid. In this hexagonal structure, the distance between two metal ions at (B) site is smaller than the distance between a metal ion at (B) site with another metal ion at (A) site.

Therefore, the conduction in M structure occurs due to hopping of charge carriers between octahedral B-sites [19]. It is reported that, Co and Ti ions having a strong preference 2b and 4f₂ octahedral sites and at higher substitutions prefer tetrahedral as well as octahedral [20]. Thus, as the replacement of Fe ions by Co and Ti ions increases up to x = 0.4, the concentration of impurities such as Fe²⁺ and Co³⁺ in octahedral B-sites increases (to keep electric neutrality in the site) this increase the hopping probability for electrons and holes between Fe³⁺ ↔ Fe²⁺ and Co³⁺ ↔ Co²⁺ respectively. The increase in the hopping probability increases the dielectric polarization, i.e. causing gradually increasing in the values of ε' and tanδ with x up to 0.4. On the other hand, it is reported that, for x ≥ 0.4 both porosity and cell volume increase with the increase, x, up to x=0.8 [7]. The increasing in porosity and the cell volume (i. e. the hopping length) can be obstructs the hopping processes or briefly decreases the dielectric constant and loss tangent for the samples with x ≥ 0.4.

IV. Conclusion

The results of this work can be summarized as follows:

- 1) The real dielectric constant decreases with increasing frequency, this result agrees with Koops model.
- 2) Tan δ showed abnormal behavior (relaxation peaks) at certain frequencies. These relaxation peaks at low frequency region is attributed to the effect of grain boundaries and take place when the jumping frequency of charge carriers become equal to that of the applied AC electric field.
- 3) With increasing Co and Ti ions substitution, ε' and tan δ increase reaching maxima at x=0.4, this was attributed to the cation distribution in the system. It is shown that for x>0.4, both ε' and tan δ decrease with increasing x, this behavior attributed to the increasing in porosity and cell volume of the samples and/or due to the change in microstructure for the samples at higher substitutions.
- 4) The activation energy for dielectric relaxation E_D was estimated according to Arrhenius relation. It is shown that E_D decreases with x up to x=0.4 after that it increases, i.e. E_D has an inverse proportional with ε' and tanδ. This give a conclusion that the higher dielectric activation energy is associated with lower dielectric polarization.

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