# Influence of Cu Addition on the Structure and Dielectric Properties of CaTiO₃

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*The structure characterization and dielectric properties were studied for a series of copper-doped calcium titanates, $Ca_{100-x} Cu_x TiO_3$, where $x =[Cu/(Cu+Ca)]\% = 0.5, 1.0, 3.0$ and $5.0$, prepared by the conventional solid state reaction method. X-ray diffraction analyses indicate that all samples belong to the orthorhombic system. Cu addition results in non linear variation of lattice parameters. As the Cu concentration increases up to $x \cong 3.0$, the lattice parameters (a, b and c) as well as the unit cell volume show an increase followed by a decrease with higher concentration of Cu ($x > 3$). Variation of lattice parameters with Cu doping is discussed based on the relative ionic radius and the filling of the present vacancies. Variation of the dielectric constant ($\varepsilon$`) and dielectric loss ($\varepsilon$``) with frequency ($100 - 2x10^6$ Hz) at different temperatures (300, 400, 500 and 600 K) was studied. It showed that pure $CaTiO_3$ has the highest $\varepsilon$` value (1200) at low frequency. On the other hand, $\varepsilon$` and $\varepsilon$`` fall to lower values by the addition of CuO. By increasing the frequency up to 50 kHz, the measured $\varepsilon$` decreased for all the samples. At low frequencies, rapid increase of $\varepsilon$` and $\varepsilon$`` is observed with raising the temperature of measurements. At higher frequencies, the dielectric properties are independent on both the frequency and temperature.*

## 1. Introduction:

Oxides with the perovskite structure are well known for their ability to produce high dielectric constants with ferroelectric property leading to many important applications. Titanates as members of the perovskite structure family are widely used as ferroelectric materials with superior dielectric properties. The properties of these materials are largely depend on the method of preparation, thermal treatments and usually modified by formation of solid solution and doping with other additive oxides. CaTiO₃ exists in two modifications; orthorhombic and cubic depending on the method of preparation. It, as one of several titanate ceramic composites, has been proposed as hosts for long term

energy converter, capacitor applications [1] as well as photoelectric and photochemical devices [2].

Furthermore, Yang [3] found that addition of Cu to Ba- or Sr- titanate can greatly enhance dielectric constant through the formation of barrier layer depending upon the temperature and time of sintering. Leonov et al. [4] added MgO and CaO to prevent change in the dielectric properties of $CaTiO_3$ as a function of heating. Gubkin [5] and Tochenaya [6] have studied the effect of addition of $CrO_3$ and $Y_2O_3$ on the crystal structure and the dielectric properties of $CaTiO_3$. They found that addition of these ions did not affect the crystal structure of $CaTiO_3$ while it increased the dielectric constant and dielectric loss. In a previous work [7], the structural study of cubic $CaTiO_3$ and those doped with trivalent $Ga^{3+}$ ($Ga_2O_3$) revealed the presence of lattice imperfection due to the incorporation of Ga ions in $CaTiO_3$. On the other hand, it was found that the dielectric and electrical conductivity properties varied largely with dopant concentration [8, 9].

This paper aims at the investigation of the influence of addition of CuO as dopant on the structural feature and the dielectric behavior of $CaTiO_3$ (CT) in a wide range of both temperature and frequency.

## 2. Experimental:

Polycrystalline samples of copper-calcium titanates of the compositional formula $Ca_{100-x}$ $Cu_x$ TiO3, where x = [Cu / (Ca + Cu)]% = 0.0 (CT), 0.5, 1.0, 3.0 and 5.0 were prepared by the well-known double sintering process at 1100 K for 16 h then at 1300 K for 16 h in atmospheric pressure [2].

X-ray diffraction analysis (XRD) was done at room temperature to determine the present phases and the structure characteristics of specimens. Philips 1710 diffractometer was used with Cu-K$\alpha$ radiation ($\lambda$ = 1.5418 Å) operated at 40 kV and 20 mA and over a wide range of Bragg angle ($20^o \leq 2\theta \leq 80^o$). The lattice parameters (a, b and c) were calculated by a least-squares method using PDP program of Calligaris [10].

Capacitance and loss tangent measurements were carried out on the samples in the form of pellets of about 11 mm diameter and 2-3 mm thickness using Hioki 3532 LCR Hi Tester instrument, Japan. The dielectric constant $\epsilon$` and dielectric loss $\epsilon$`` were calculated as a function of frequency (100 - $2 \times 10^6$ Hz) at different temperatures of 300, 400, 500 and 600 K.

## 3. Results and Discussion:

The XRD diffractograms of a pure and CuO-doped $CaTiO_3$ samples are shown in Fig. (1). It was found that all the observed d-value fit those of orthorhombic system (PDF-No 42-423). It is worthy to state that all diffracted lines of the cubic system (PDF-No43-226) are very close to some of those of the orthorhombic system. So that, if a fraction of the cubic system is present, it is very difficult to prove its existence. Therefore, the prepared samples were identified as orthorhombic system. Effect of Cu addition on the calculated lattice parameters as well as on the unit cell volume is depicted in Fig. (2). The effect of doping can be discussed in the light of the ionic radii of $Cu^{2+}$ (0.70 Å), which may substitute $Ca^{2+}$ (0.06 Å), $Ti^{2+}$ (0.80 Å) or $Ti^{4+}$ (0.64 Å), or the presence of lattice defects (vacancies). In case of low Cu additions (x < 3.0), $Cu^{2+}$ may substitute $Ti^{4+}$ or filling the vacancies causes an increase of the lattice constants and, consequently, expansion of the unit cell. On the other hand, high Cu concentration (x > 3), $Cu^{2+}$ may replace $Ca^{2+}$ and / or $Ti^{2+}$, which results in a decrease of the lattice constants that caused shrinkage in the unit cell.
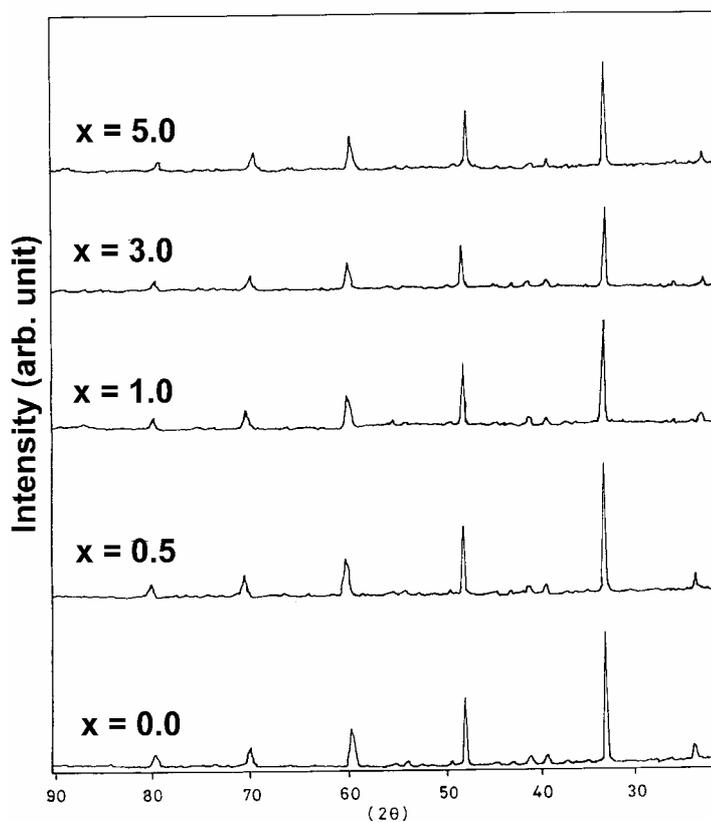


**Fig. (1):** X-ray diffractograms of pure and Cu-doped $Ca_{100-x} Cu_x TiO_3$.
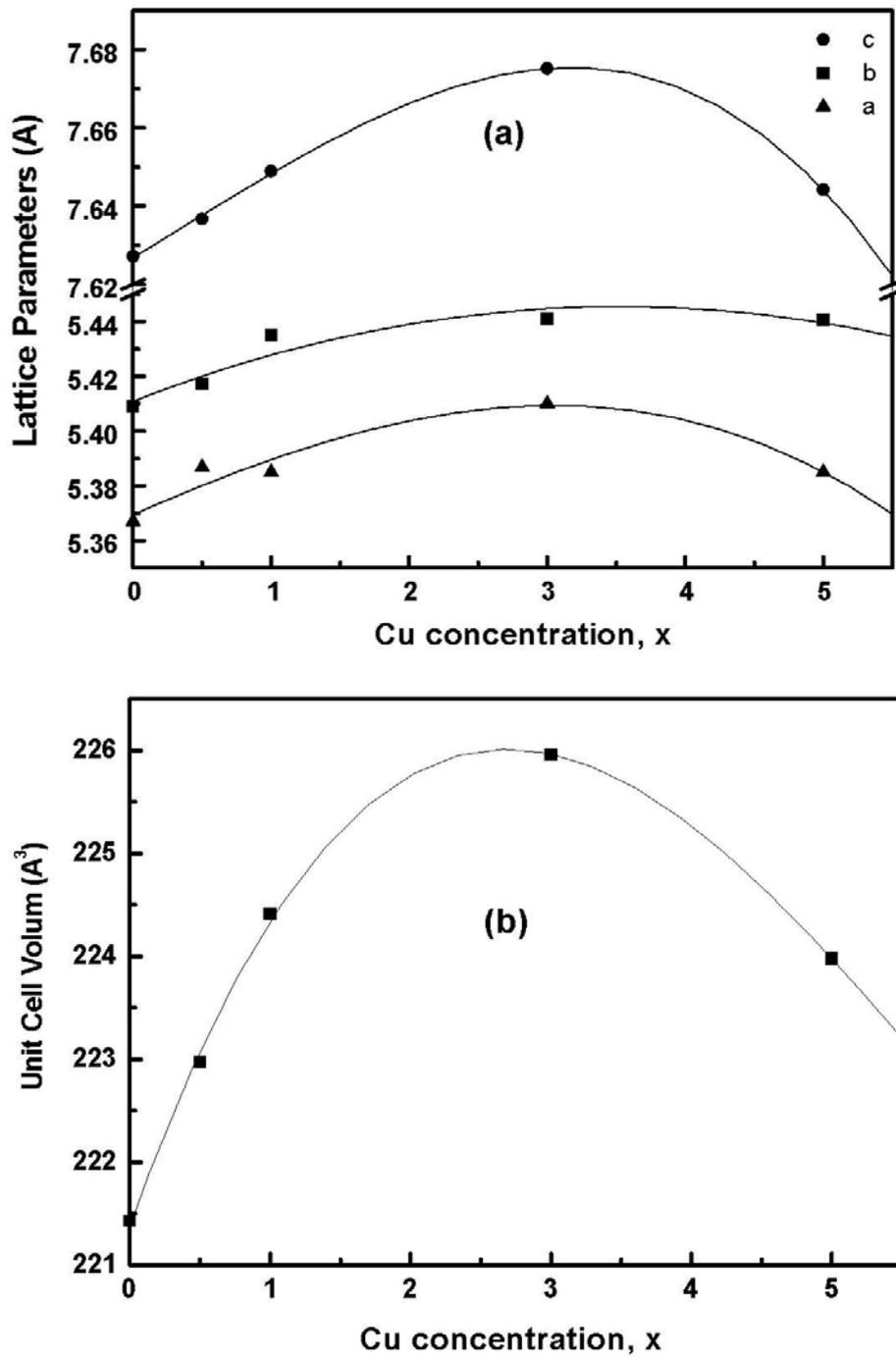
**Fig. (2):** Variation of (a): lattice parameters and (b): unit cell
volume as a function of Cu concentration.

Figure (3) illustrates the experimental dielectric constant data for the samples of various copper concentrations as a function of frequency at different temperatures. The relative permittivity shows dispersion with frequency for all the samples. In the low-frequency region, the value of $\varepsilon`$ is very high and its value decreases with the increase in the Cu-ion concentration. On the other hand, the value of $\varepsilon`$ is nearly frequency independent at the higher frequencies. Moreover, its value is not as sensitive to Cu-concentration as observed at lower frequencies. The frequency dependence of $\varepsilon`$ at different temperature shows that at high frequencies; the dielectric constant values are almost temperature independent but as the frequency decreases (50kHz), its value becomes more temperature sensitive. Similar results have been reported earlier [8].
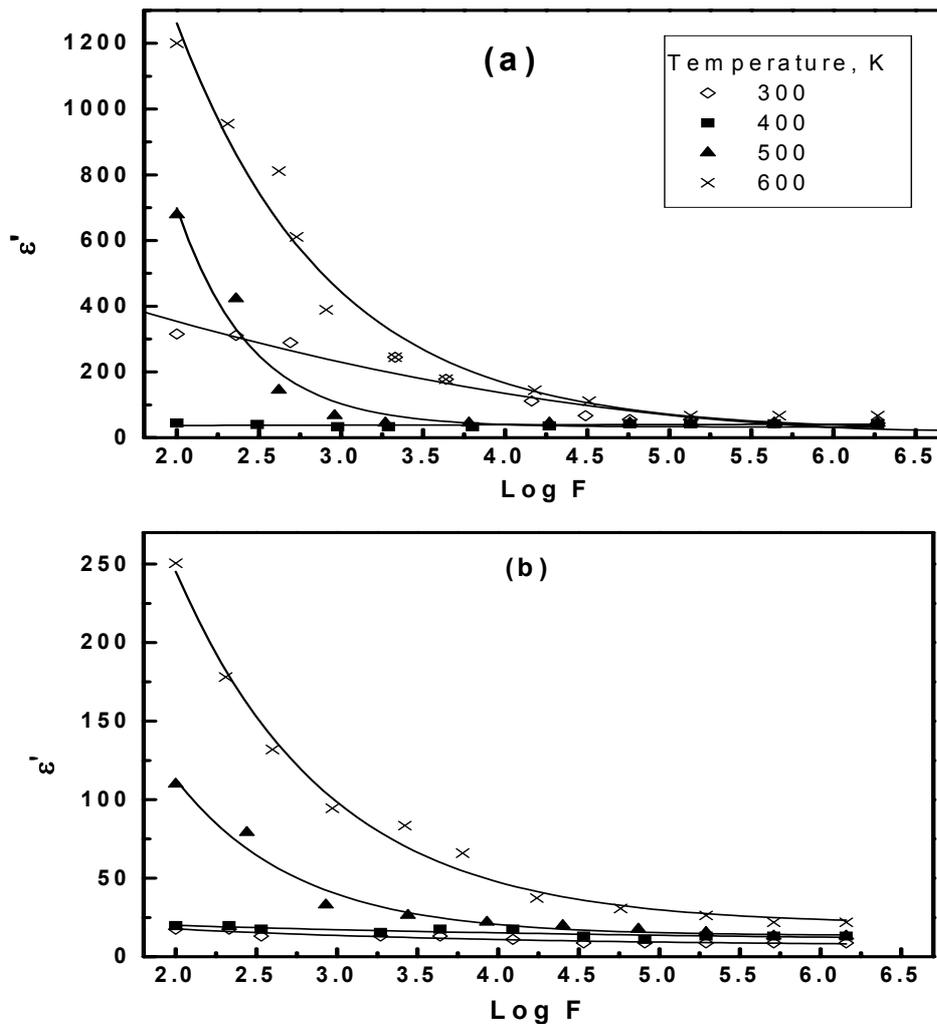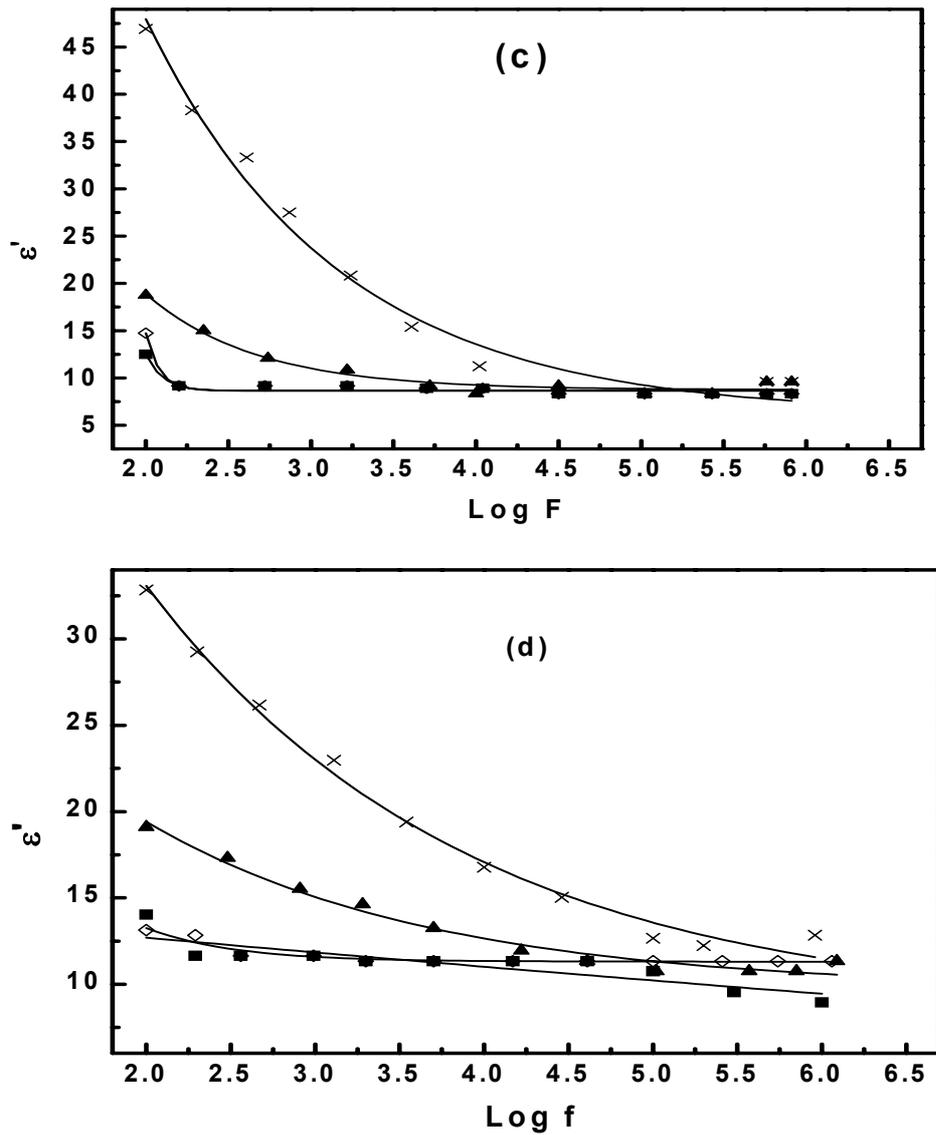
**Fig. (3):** Variation of dielectric constant ε' as a function of frequency
at different temperatures of $Ca_{100-x}$ $Cu_x$ $TiO_3$: (a) x = 0.0,
(b) x = 0.5, (c) x = 3.0 and (d) x = 5.0.

The observed dispersion in the dielectric constant–frequency relation can be explained on the bases of Maxwell-Wagner model [11] in which the solid is assumed as composed of well conducting grains separated by the poorly

conducting grain boundary. In case of Cu-free sample (CT), dispersion can be explained on the basis that the available Ti ions on the octahedral sites give rise polarization to the maximum possible extent at low frequencies. As the applied frequency is increased, the polarized Ti ions in the titanate material could not follow the alternating field and a lag in orientation polarization arise lead to a decrease in the dielectric constant.

The decrease of ε` with Cu-ion dopant addition, according to McChesney et al. [12] and Cook and Tennery [13] was attributed to the formation of weak ferroelectric layers at the grain boundaries of the base-CT. These boundary layers are assumed to be compositionally different from the interior of the grain and may arise as a result of the reaction between Cu ions and CT or may originate from Cu-Ca-Ti complex oxides segregation at the grain boundaries. In higher doped sample, Cu ions inhibit the effect of Ti ions and decrease their total number and the number of space charge carriers decreases leading to a lower polarization and, hence, a lower dielectric constant.

A similar type of variation is also observed in the dielectric loss of both the pure CT and the copper doped samples as shown in Fig. (4). ε`` decreases up to approximately the same frequency (50kHz) as ε`, after which, it remained almost constant. This type of variation of ε` and ε`with frequency is a feature of semi-conducting materials.

It can be noted that pure CT has the highest ε` (1200) ε`` (580) values at lower frequencies. The high dielectric constant in Ca, Ba or Sr titanates at low frequency, according to Subramanian et al. [14] is generally attributed to rattling of $Ti^{4+}$ within its $TiO_6$ octahedron where the Ti-O bonds were put under tension and polarizablity of $TiO_6$ of the octahedron increased. On doping ε` and ε`` decrease vigorously from few hundreds at x= 0.5 down to few tens at x = 5.0. In case of increasing temperatures, ε`and ε`increases in consequence.

The rapid increase in ε` at lower frequencies with temperature can be explained by the superionic nature and spontaneous polarization of samples due to motion of $Ti^{4+}$, $Ca^{2+}$ and $Cu^{2+}$ cations. In general, increasing of ε` with temperature could be attributed to the fact that these perovskite samples possess polar dielectric in which the orientation of electric dipoles is facilitated with temperature where ε` increases in consequence. Temperature also increases the effect of environment that enhances the ease of polarization of flexible polar bounds in the crystal lattice.
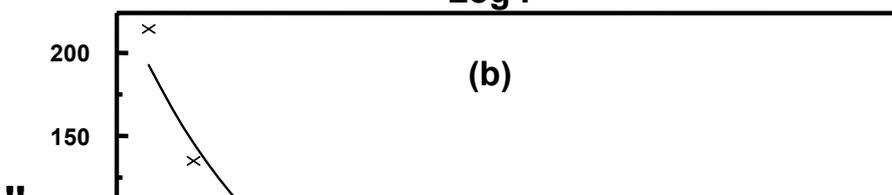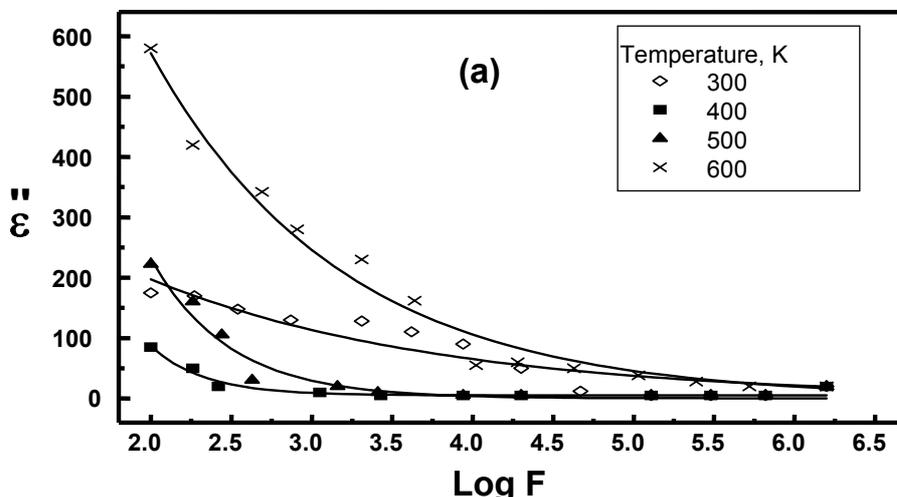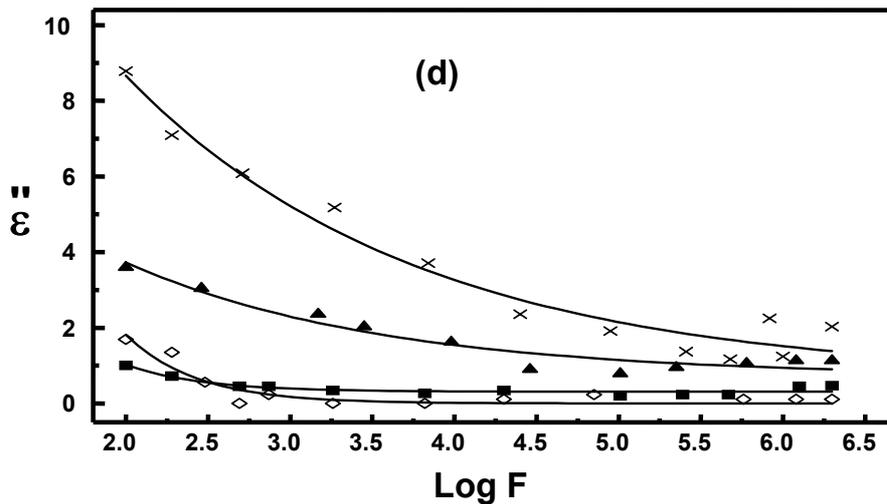
**Fig. (4):** Variation of dielectric loss $\varepsilon''$ as a function of frequency at
different temperatures of $Ca_{100-x}$ $Cu_x$ $TiO_3$: (a) x = 0.0,
(b) x = 0.5, (c) x = 3.0 and (d) x = 5.0.

## 4. Conclusions:

X-ray diffraction data revealed the presence of the orthorhombic phase
of calcium titanate and complete absent of any Cu-phase. Variation of lattice
parameters and unit cell volume with Cu doping seems to be due to the
difference in radius of the constituent ions and as a result of reduction of lattice
imperfection (vacancies). Measurements in a wide range of frequency and
temperature prove the effect of Cu doping on the dielectric behaviour of
$CaTiO_3$. At lower frequency, the dielectric properties are greatly affected by Cu
addition as well as the measuring temperature. Both $\varepsilon'$ and $\varepsilon''$ decrease with Cu
addition or descending of temperature.

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