CHAPTER 9

THE EFFECT OF CeO_2 DOPING ON THE DIELECTRIC PROPERTIES OF $CaCu_3Ti_4O_{12}$ CERAMICS PREPARED VIA VIBRO-MILLING METHOD

9.1. Introduction

$CaCu_3Ti_4O$ (CCTO) has attracted a significant amount of attention base on dielectric properties, with has a large dielectric constant of 10,000 to 100,000 and is independent of temperature over the range of 100-400K [17, 72, 92]. These properties make it applicable to a variety of microelectronic device applications for capacitive elements [17]. CCTO has a complex cubic perovskite like structure with a lattice parameter, a~7.393 Å [15]. The explanation of high dielectric constant of CCTO was first proposed by Subramanian *et al.*, in terms of local dipole moments associated with off-center displacement of Ti ions [92]. Change in dielectric constant of CCTO has been wildly related to its microstructure [44]. It is also reported that electrical properties of CCTO depends on many factors such as processing conditions, doping, and chemical stoichiometry. Many works reported that dielectric responses of CCTO are strongly affected by dopants (La, Mn, Zr, Co, Fe, Ni, Sc and Nb etc.)[34-36, 73-74]. However, effects of Ce doping at A-site of CCTO on the dielectric response have not been investigated. In the present work, the dielectric properties of CCTO ceramics modified by CeO_2 have been studied. The electrical properties of the Ce modified CCTO were reported.

9.2. Experimental procedure

The $CaCu_3Ti_4O_{12}$ (CCTO) powder was prepared by using solid state synthesis methods. High purity (> 99.9%) $CaCO_3$ (Riedel-de Haen), TiO_2 (Riedel-de Haen) and CuO (Aldrich) powders were mixed and milled in ethanol using a vibratory mill for 6 h. For the doping study, CeO_2 powders were added to CCTO at the calcination stage based on the stoichiometry in concentrations of 1.0 and 2.0 mol %. Each batch was then calcined in air at 900 ^{o}C for 2 hours. After milling and calcination, the calcined powder was granulated using polyvinyl alcohol (PVA) 3% binder and formed under a uniaxial pressure of 2,000 kg/cm^2 into discs, typically 10 mm in diameter and 2 mm in thickness. The discs were sintered in air at 1,100^{o}C for 4 hours in a step of 5^{o}C/min. The obtained samples were polished to produce the flat uniform surfaces. All the samples were characterized by x-ray diffractometer (Bruker D8 Discover) at room temperature using CuK_{α} radiation as the x-ray source. Silver paste was applied on the sample surfaces as the electrical contact. The painted samples were dried at 750 ^{o}C for 20 minutes. The polished ceramics were observed using SEM (JEOL JSM-5910LV) to study the microstructure. The dielectric constants and loss tangents against temperature were measured at the frequency of 100 Hz - 500 kHz (using Agilent 4284A LCR meter).

9.3. Results and discussion

The XRD result for the ceramic samples is shown in Figure 9.1. All the peaks were matched with the stand pattern of CCTO, based on the data in the Inorganic Crystal Structure Database (ICSD) file No.032002. No impurity or raw materials peaks were observed, under the limit of XRD detection. The lattice constants of all ceramic samples were determined and were found to be in the range 7.371- 7.3372 Å, which is close to the ICSD standard data (7.371 Å).

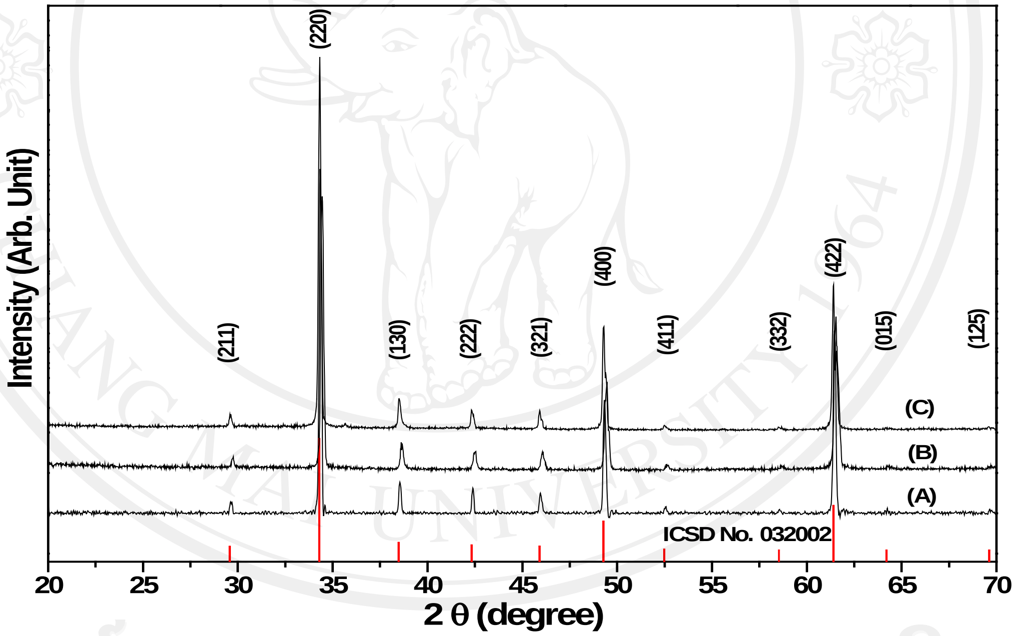


Figure 9.1 XRD patterns of pure and doped CCTO: (A) Undoped,

(B) 1.0 mol% Ce and (C) 2.0 mol% Ce .

The lattice constant (Å) as a function of Ce content is shown in Figure 9.2. The lattice constant slightly increased as the amount of CeO_2 increased. This implies that Ce ions could go into solid solution with the CCTO lattices.

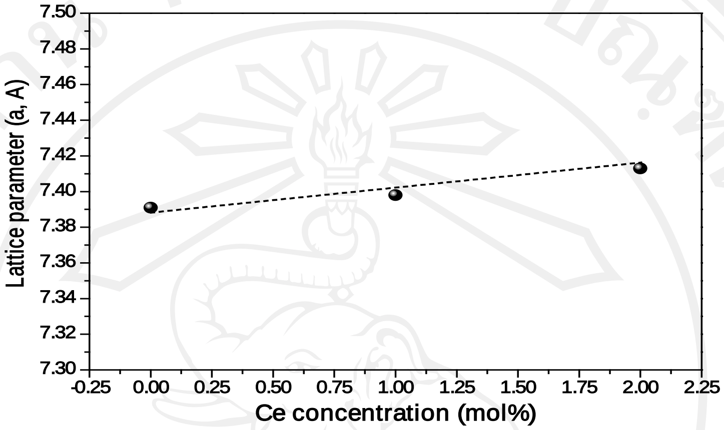


Figure 9.2 Lattice constant of doped CCTO ceramics as a function of Ce concentrations.

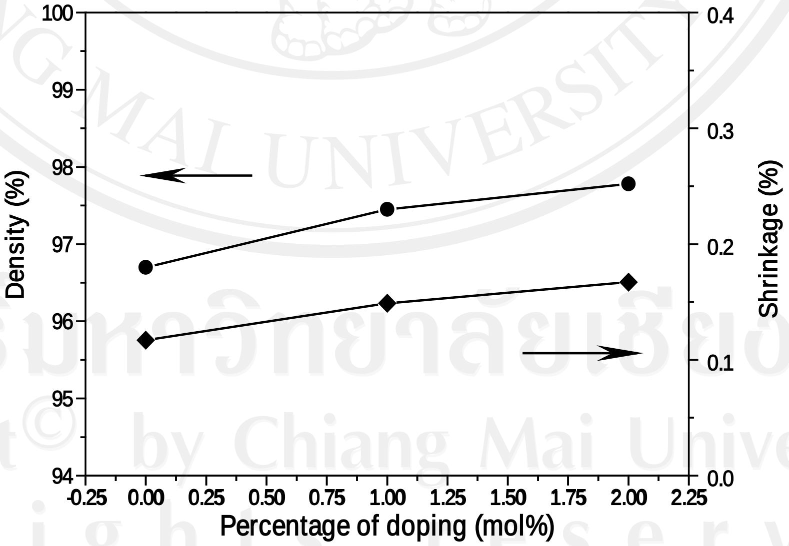
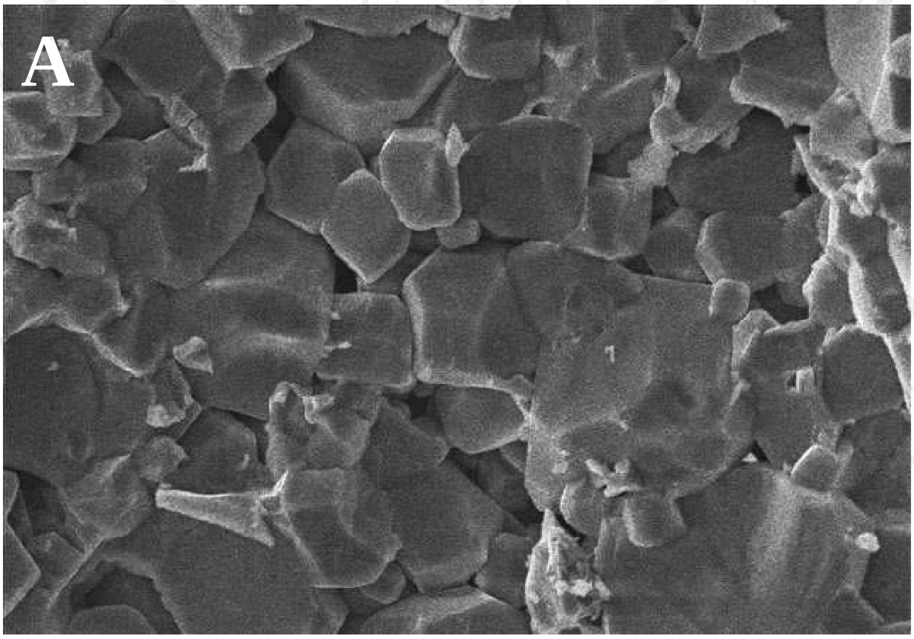


Figure 9.3 Density and shrinkage of doped CCTO ceramics versus Ce concentrations.

In addition, density and shrinkage slightly increased with the concentration (Figure 9.3), suggesting that the doping oxide help to promote the densification.

Fractured surfaces of the CCTO ceramics (undoped and doped 2.0 mol% Ce) are displayed in Figure 9.4. CeO_2 doping produced a notable decrease in grain size. Average values of grain size, as measured by the linear intercept method, decreased from ~ 20.4 μm for unmodified CCTO to ~1.9 μm for all modified CCTO samples. Hence, CeO_2 doping inhibited grain growth. Furthermore, it may assumed that some of Ce ions cannot substitute into the lattice of CCTO, giving rise to a segregation of doping oxide which forms secondary phases on a very small scale at the grain boundaries without the detection by XRD. The trend of the grain size also matches that of the degree of crystallinity as larger grain size is, higher degree of crystallinity is obtained.



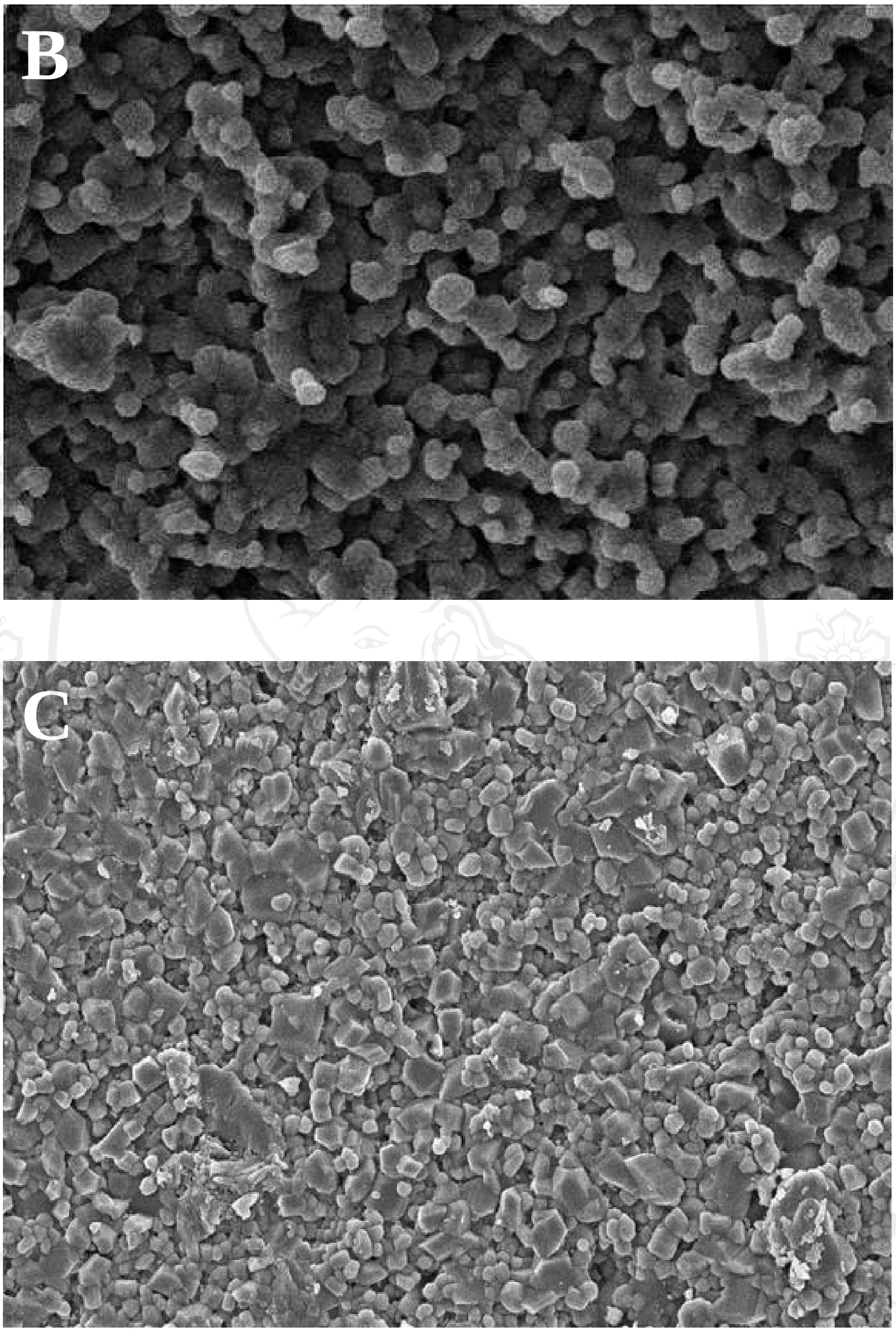
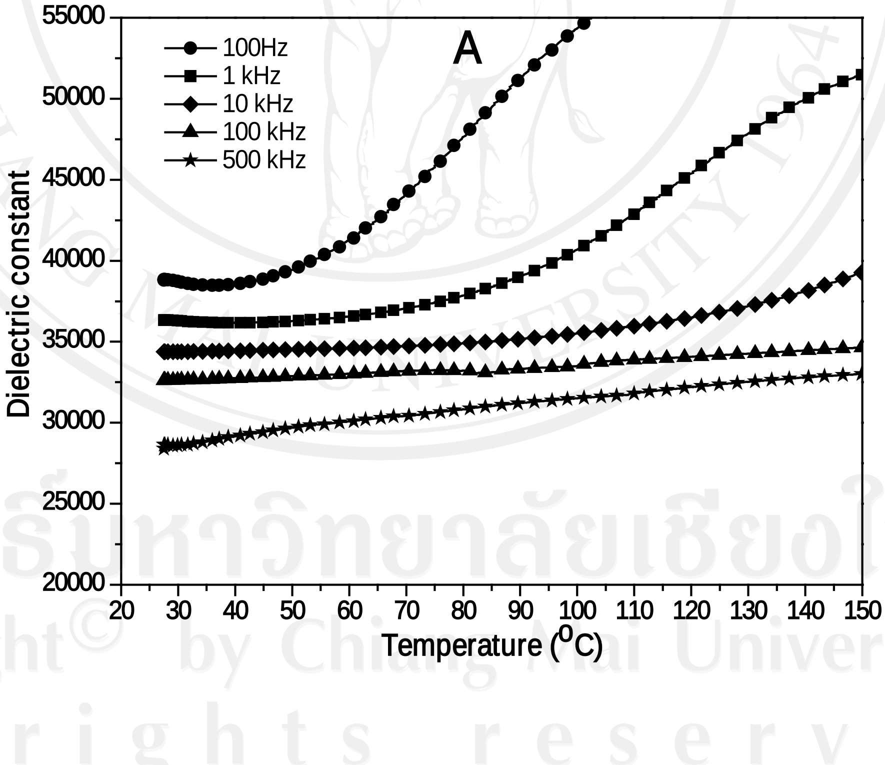


Figure 9.4 Fracture surfaces of selected samples: (A) pure CCTO , (B) Ce 1.0 mol% doped CCTO and (C) Ce 2.0 mol% doped CCTO.

The temperature dependences on dielectric constant, calculated dielectric constant, dielectric loss and calculated dielectric loss at various frequencies of the ceramic samples are presented in Figure 9.5 and 9.6, respectively. For the unmodified CCTO, at temperature less than ~60 ^{o}C, the dielectric constant exhibited a stronger dielectric-frequency dependent while the doped samples showed a weaker frequency dependent. At temperature higher than ~45 ^{o}C, all samples exhibited a strong dielectric -frequency independent.



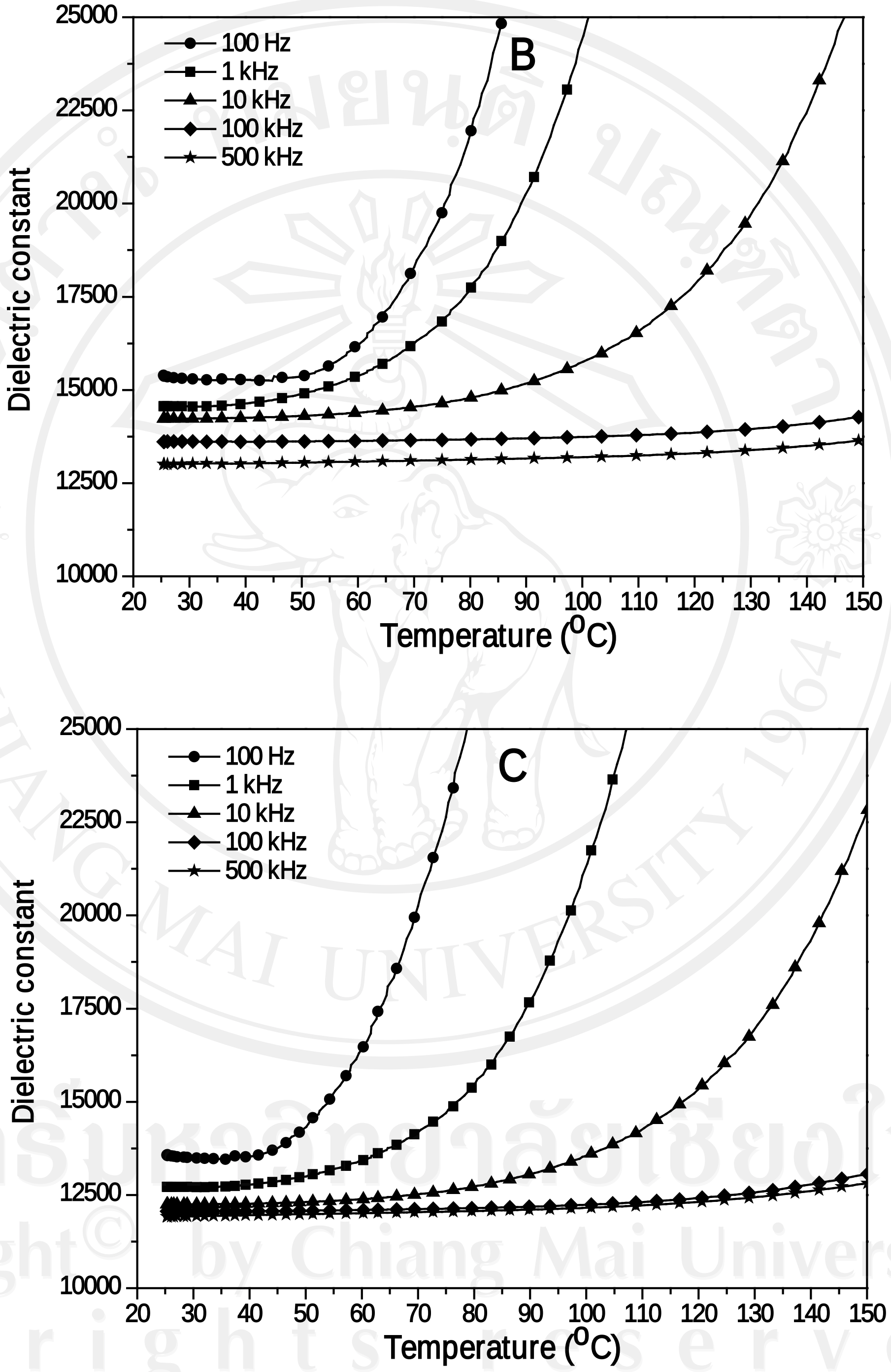
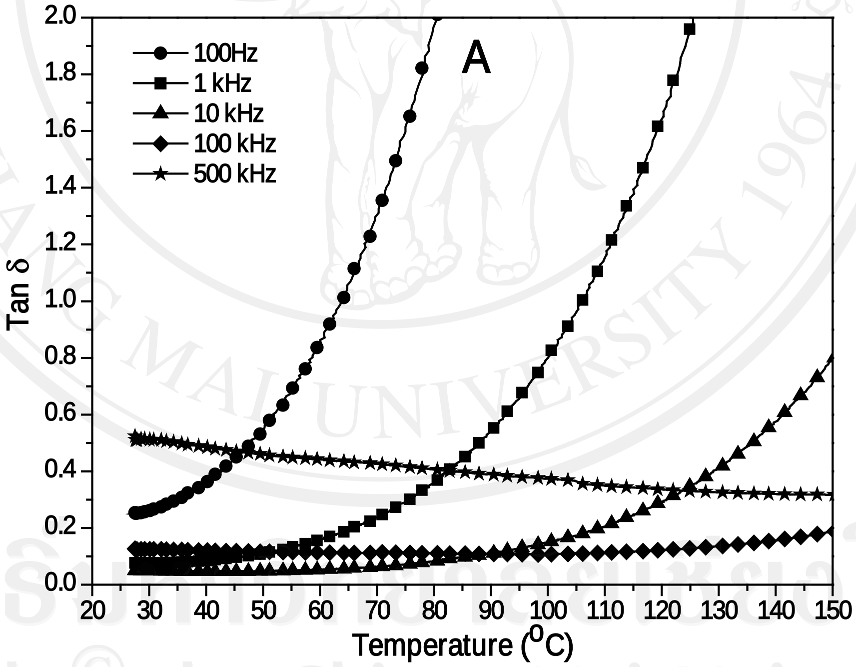


Figure 9.5 Dielectric constant as a function of temperature for the samples: (A) Undoped CCTO, (B) Ce 1.0 mol% doped CCTO and (C) Ce 2.0 mol% doped CCTO

It should be noted that at high frequency, all samples showed a dielectric independent of temperature. The dielectric constant at room temperature and at 100 kHz decreased from 32,500 for the unmodified sample to 12,000 for the 2.0 mol% sample. Similar results have been observed for many modified CCTO ceramics [34, 74]. However, the doping improved in the loss tangent performance (Figure 9.6 (C)). The loss tangent at room temperature and at 100 kHz decreased from 0.13 for the unmodified sample to 0.03 for the 2.0 mol% sample while at 500 kHz, it decreased from 0.52 for the unmodified sample to 0.05 for the 2.0 mol% sample.



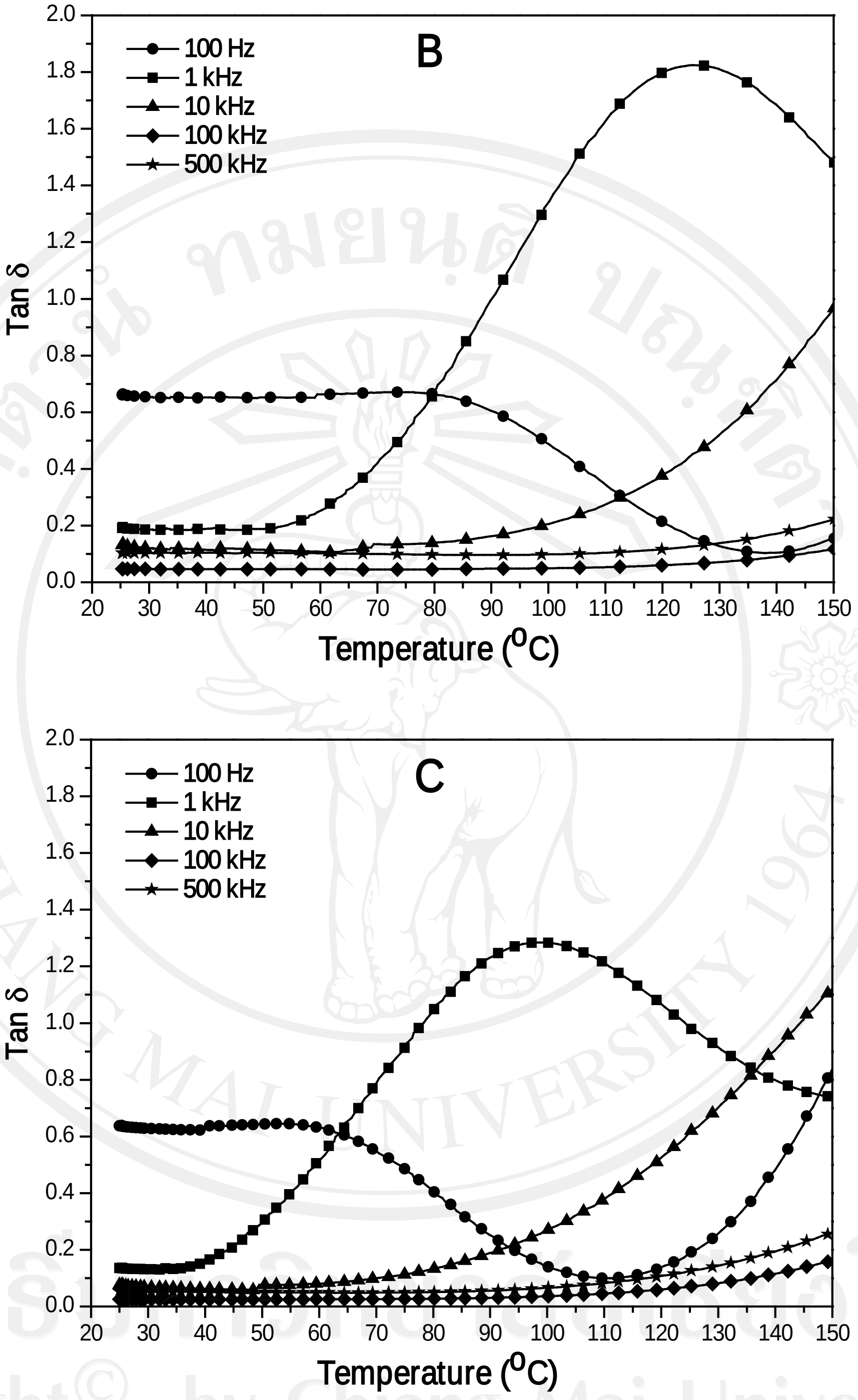


Figure 9.6 Loss tangent as a function of temperature of the samples: (A) Undoped CCTO, (B) Ce 1.0 mol% doped CCTO and (C) Ce 2.0 mol% doped CCTO

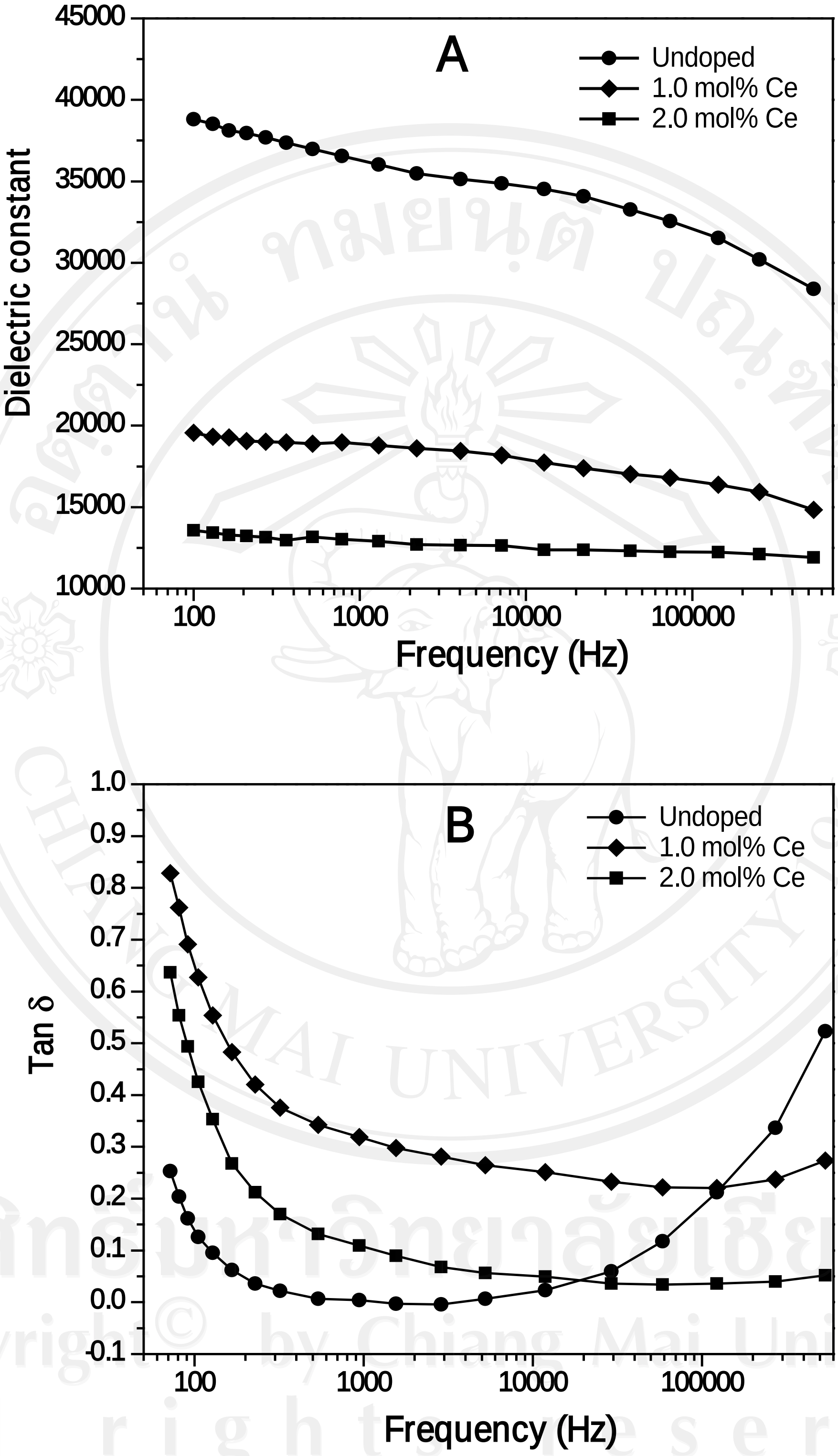


Figure 9.7 Dielectric properties of the samples as a function of frequency:

(a) dielectric constant and (b) loss tangent.

Plots of the dielectric constant and loss tangent as a function of frequency at room temperature are illustrated in Figure 9.7. The Ce doping produced a lower in loss tangent. However, at a lower frequency and a higher frequency, a higher loss tangent was observed.

From the internal barrier layer capacitor model (IBLC), the equivalent circuit of CCTO system can be consisted of two parallel RC elements connected in series. The two parallel RC circuits represent to semiconducting bulk grain (which consists of grain resistor (R_g) and grain capacitor (C_g)) and insulating grain boundary(which consists of grain boundary resistor(R_{gb}) and grain boundary capacitor (C_{gb})). In case $R_{gb} >> R_g$ and $C_{gb} \sim C >> C_g$ and $\omega R_b C_b << 1$, the loss tangent can be express as [76]:

$$\tan\delta = \frac{1}{\omega R_{gb} C} + \omega R_g C \quad (1)$$

The first term is dominated at low frequency, therefore the loss tangent decreased with increasing frequency. However, at high frequency the second terms become dominate. Thus, the loss tangent increased with the frequency.

For CCTO system, the dielectric behavior could be rationalized using the following equation [89, 90]:

$$\varepsilon_s' = \frac{C_{gb}}{C_0} \quad (2)$$

Where ε_s' is the static dielectric constants and C_0 is the empty cell constant.

It was also proposed that the apparent dielectric constant (ε'_r) can be related the grain size (*d*) and the thickness of grain boundary (barrier width, *t*) and internal dielectric constant of the barrier material (ε_{gb}) as the below expression:

$$\varepsilon'_r = \varepsilon_{gb}(\frac{d}{t}) \tag{3}$$

In the case of Ce doped samples, it is believed that the Ce ions had more interaction at the grain boundary than at the bulk grain. This may cause an increase in barrier width and change in ε_{gb} as a result of the reduction of dielectric constant. For the Ce doping, the reduction in dielectric constant can be associated to the decrease in grain size. In addition, defect and second phase at grain boundary could be induced after doping. These factors may be contributed to the reduction in the dielectric constant

9.4. Conclusions

Dielectric properties of pure CCTO and Ce doped CCTO were reported in this article. The doping produced the reduction of dielectric constant. However, the better loss tangent performance was observed after doping. The loss tangent – frequency characteristic at room temperature was agreed with the IBLC model.