CHAPTER 5

DIELECTRIC PROPERTIES OF $CaCu_3Ti_{4-x}Mn_xO_{12}$ CERAMICS

5.1. Introduction

The perovskite - type compound $CaCu_3Ti_4O_{12}$ (CCTO), was first synthesized by Bochu et al. [15]. This titanate oxide crystallizes in a cubic structure with *Im*3 space group. The TiO_6 octahedra are tilted, resulting in the doubling of the perovskite-like lattice parameter and involves a square planar arrangement of the oxygen around the Cu^{2+} cations. [12,67]. The dielectric constant is almost temperature independent from 200 K to 400 K, with low frequency dielectric constant of CCTO can be as high as 95,000 in single crystals , and 12,000 in sintered pellets [12, 44]. For the ceramic [12] and thin-film [43] samples at room temperature, the typical value of tan δ is about 0.2 at 10 kHz.

The high dielectric constant of CCTO can then be understood based on a barrier layer mechanism. This is a well-known mechanism for titanates that are processed in such a way as to produce grains that are reduced and conducting when coupled with grain boundaries that are oxidized and much less conducting [12].

The partial substitution of divalent Ca^{2+} by the trivalent La^{3+} was carried out, in order to increase the conductivity of the grains [6].The loss angle can be reduced by adding of some elements such as manganese oxide (MnO_2) [68]. In this work we extend the study on CCTO samples with substitutions of Ti ions by Mn ions leading to the formula $CaCu_3Ti_{4-x}Mn_xO_{12}$, ranging from x = 0.08 up to 0.40. Characterization of the samples was carried out using x-ray diffraction (XRD) and scanning electron microscopy (SEM). Other physical properties such as, density, dielectric constant and loss angle were intensively studied.

5.2. Experimental procedure

The $CaCu_3Ti_4O_{12}$ (CCTO) powder was prepared by the mixed-oxide route. High purity (> 99.9%) $CaCO_3$ (Riedel-de Haen), TiO_2 (Riedel-de Haen) and CuO (Aldrich) powders were weighed in an appropriate ratio, fully mixed by ball milling for 24 h using zirconia balls in ethanol media. After being dried, the powders were calcined at 850^{o}C for 2 h to form the CCTO powder. In searching for the most appropriate sintering temperature, the calcined powder was granulated using polyvinyl alcohol (PVA) 3% binder and formed under a uniaxial pressure of 1500 kg/cm^2 into discs, typically 15 mm in diameter and 2 mm in thickness. The discs were sintered in air at 850 - 1050^{o}C in a step of 50^oC (with soaking time of 2 h). The ramping and the cooling rates were 300^oC/h. The XRD and density results showed that the most appropriate sintering temperature of CCTO was 1000^oC. The substituted CCTO samples was prepared by mechanically ground (24 h) mixtures of the calcined CCTO powder and various amounts of $MnCl_2.4H_2O$ powders, leading to the formula $CaCu_3Ti_{4-x}Mn_xO_{12}$ (x = 0.08, 0.16, 0.24, 0.32 and 0.40). The mixtures were formed into discs employing the same process as that of the undoped samples. The discs were sintered in air at 1000^oC for 2 h, with the same ramping and the cooling rates. During sintering oxygen gas was fed into the furnace at the rate of 100 c.c./min. The discs were polished to produce the flat uniform surfaces. All the samples were characterized by x-ray diffraction (JEOL JDX-8030) at room temperature using CuK$_\alpha$ radiation as the x-ray source. Silver paste was used as the electrical contact. The painted samples were dried at 750 ^{o}C for 20 minutes.

The polish 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 1 kHz (using HP 4192A LCZ meter).

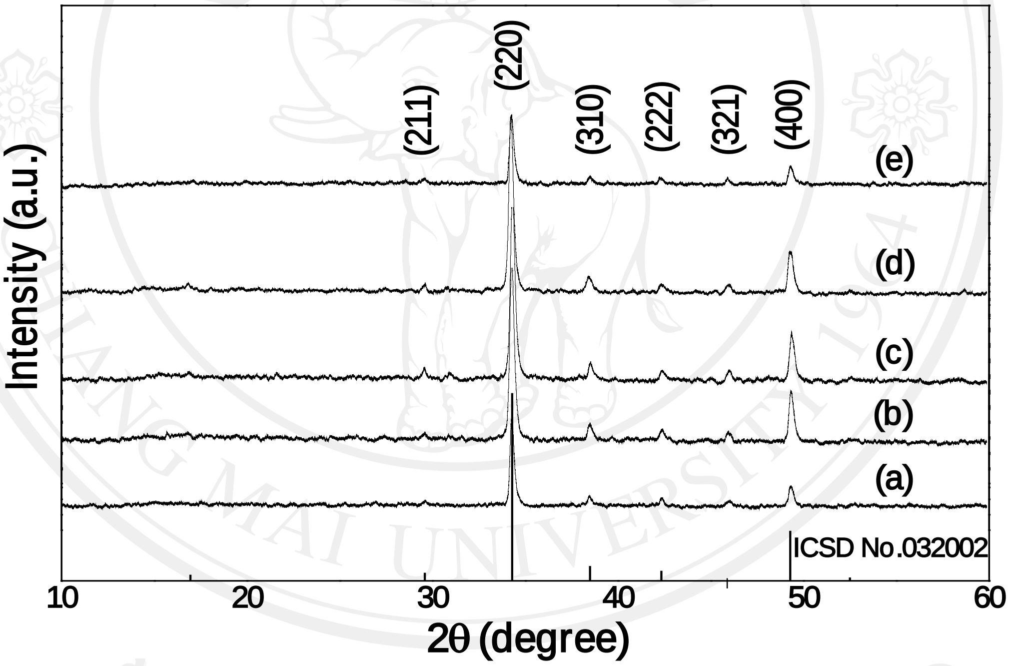

Figure 5.1 Powder XRD results of CCTO ceramic samples, at various sintering temperatures. (a) 850°C/2 h, (b) 900°C/2 h, (c) 950°C/2 h, (d) 1000°C/2 h, and (e) 1050°C/2 h.

5.3. Results and discussion

Figure 5.1 shows the x-ray diffraction results for the CCTO ceramic samples at various temperatures. All the peaks can be attributed to CCTO, based on the data in the Inorganic Crystal Structure Database (ICSD) No.032002, having the lattice parameter (a) of 7.37 Å. It can be seen that the CCTO phase started to form at 850°C and most pronounced at 1000°C, whilst sintering at 1050°C yielded relatively lower intensity of the main peaks (220), indicating lower content of CCTO. Furthermore, the samples melted at the highest sintering temperature (1100°C).The density results of the calcined powder also showed that the highest density was obtained at 1000°C (data not shown here). This is in agreement with our XRD results and that of Yang et al.[58] and Brize et al.[59].

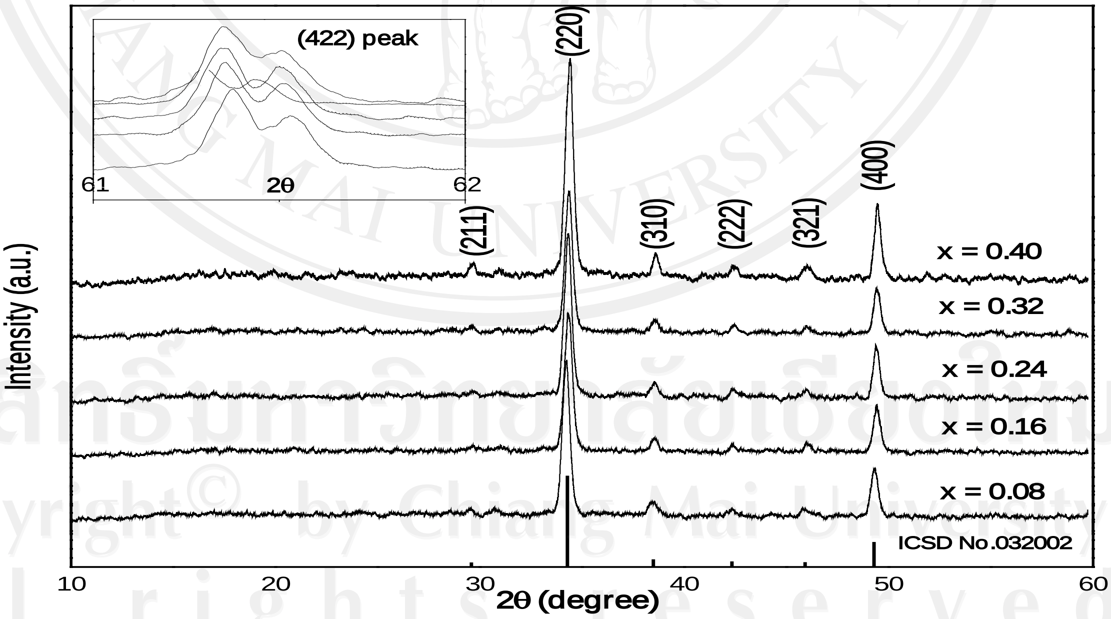

Figure 5.2 Powder XRD results of $CaCu_3Ti_{4-x}Mn_xO_{12}$. The top left inset is an expanded view of the XRD patterns around 2θ = 61.4°.

The XRD results for the Mn-doped CCTO samples were presented in Figure 5.2. All the peaks can be well indexed using the same data base (ie.ICSD No.032002). The lattice constants and the densities of the ceramics were tabulated in Table 5.1. The lattice constants were obtained by a least-squares fit method. They were found to slightly increase with the increasing x, indicating that Mn does enter the lattice. When x = 0.24 the lattice constant tends to saturate, suggesting that the Mn solubility limit at x~0.24 (please also see Table A). The top left inset of the figure is an expanded view of the XRD pattern around 2θ = 61.4^o, showing the shift of the (422) peaks. The lower intensity peaks come from the $CuK_{\alpha 2}$ radiation. The increase of the lattice constant is probably due to the fact that Mn ion has larger ionic radius than Ti ion. In general, the practical frequency employed in capacitor applications is around 1 kHz, though the CCTO system is frequency dependent.

TABLE 5.1 Percentage of the density and the lattice parameter (a) of the Mn-doped CCTO

$CaCu_3Ti_{4-x}Mn_xO_{12}$ (x values)	Density* (%)	lattice parameter a (Å)
0	94.05	7.370
0.08	93.17	7.396
0.16	92.85	7.398
0.24	91.77	7.403
0.32	91.65	7.403
0.40	90.96	7.403

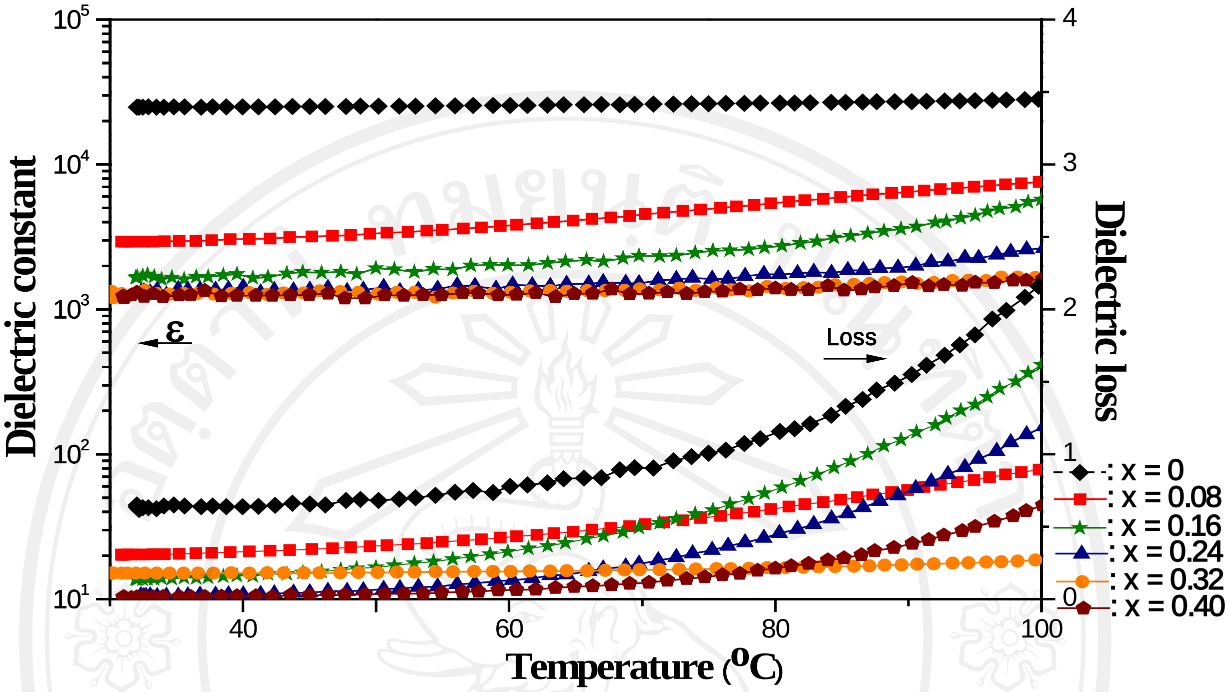

Figure 5.3 Temperature dependence of the dielectric constant and loss tangent for the $CaCu_3Ti_{4-x}Mn_xO_{12}$ sample, sintered at 1000°C/2h and measured at frequency 1 kHz.

Figure 5.3 shows the dielectric constant and dielectric loss of Mn doped CCTO, against the temperature ranging from room temperature to 100°C. As can be seen, at the room temperature, the dielectric constant (ε_r) decreases from 15000, with the increasing x and ε_r tends to be stable (about 1200) when $x \geq 0.24$. This trend agrees well with the lattice constant results in Figure 5.2 (please also see at Table 5.1).

Besides, the ε_r is rather constant with the temperature. The dielectric loss (tanδ) does decrease with the increasing x as generally expected. The highest and lowest values were 0.7 (for x=0) and 0.06 (for x= 0.24), respectively (at room temperature). This is slightly below that obtained by Feng et al.[36], who worked on La doped CCTO system. The decrease of ε_r and tanδ may be due to the fact that during sintering there was a supply of oxygen gas in the system. Similar result was also observed by Schmid and Mader [69]. Thus there is a probability that Mn^{2+} (from $MnCl_2.4H_2O$) could be oxidized to Mn^{4+} and could substitute the Ti^{4+} lattice site, leading to the formula of $CaCu_3Ti_{4-x}Mn_xO_{12}$. This may cause the reducing of Ti vacancies, and therefore the conductivity of the ceramic decreases. However, the oxidation of Mn^{2+} to Mn^{3+} also could not be neglected. Mn^{3+} can behave as acceptors for electrons liberated from oxygen vacancy traps and thus prevent them from entering the conduction band. Nevertheless, at x = 0.24, the tanδ increased up to 1 against that of undoped (~2) at 100^{o}C. Figure 5.4 shows the SEM micrographs of the crack surface of Mn doped CCTO samples sintered at 1000^{o}C. As can be seen that the undoped sample (Figure 5.4. A), the grain size of the CCTO sample was quite high (~10μm) with small pores scattered around the grains. This may be due to melting and abnormal grain growth. Similar result was also observed by Mohamed et al. [70].

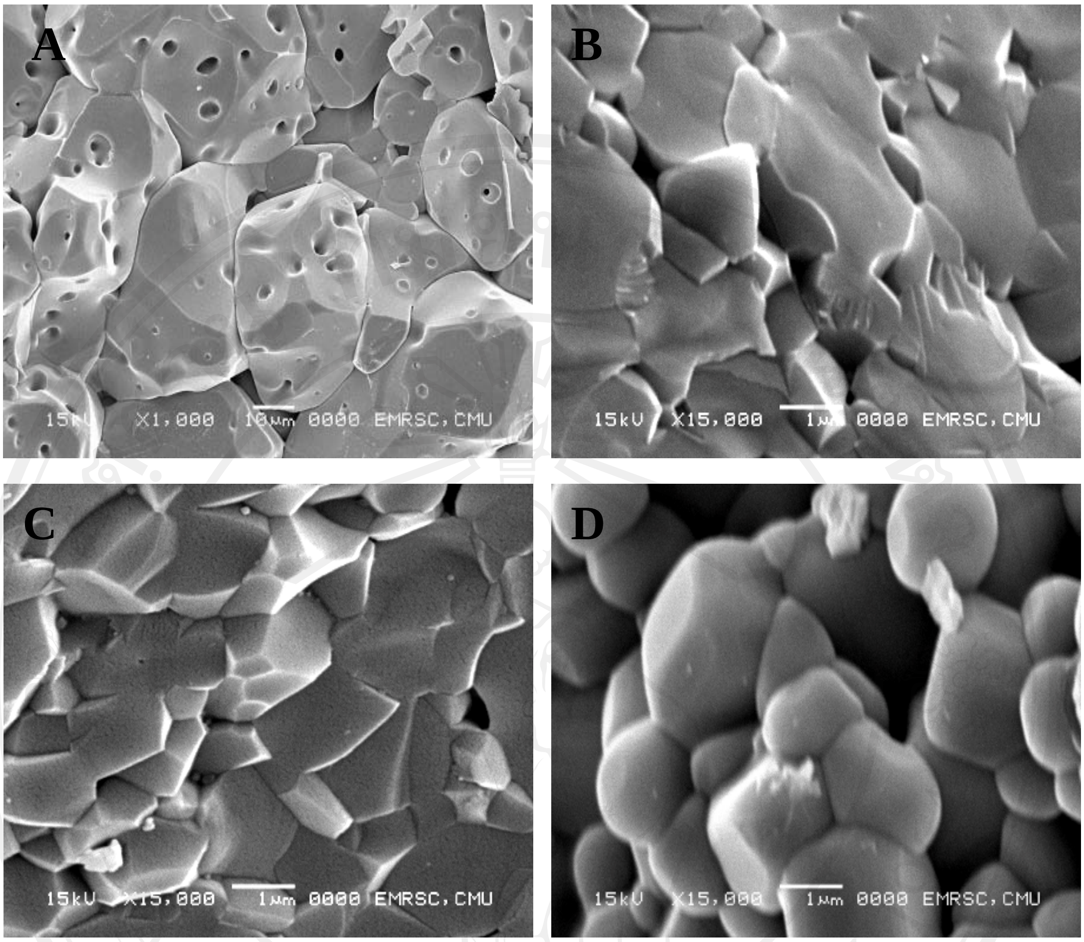

Figure 5.4 SEM pictures of the crack of $CaCu_3Ti_{4-x}Mn_xO_{12}$ sintering at 1000^oC for 2 h. Samples A: x = 0, B: x = 0.08, C: x = 0.24, and D: x = 0.40.

However, the dielectric constant of CCTO ceramics was higher than that of CCTO ceramics sintered at 1035^oC for 3h as revealed by Fang and Shiau [71]. Microstructural analysis also revealed that the grain size of the samples produced notable decrease, as measured by the lines intercept method, decreased from ~ 10µm for undoped sample to ~ 2.5µm for $CaCu_3Ti_{3.76}Mn_{0.24}O_{12}$ sample (Figure 5.4. B and

C). However, at x = 0.40 (Figure 5.4. D) pores were seen around the grains and this may affect the reducing of the dielectric constant.

5.4. Conclusions

The effects of Mn doped on the dielectric constant (ε_r), dielectric loss (tanδ) of $CaCu_3Ti_{4-x}Mn_xO_{12}$ (x = 0, 0.08, 0.16, 0.24, 0.32 and 0.40) were examined. Dielectric constant and dielectric loss (at 1 kHz) were investigated at room temperature and 100^{o}C. For x = 0.24 sample, the tanδ was found to increase from 0.06 (at room temperature) to 1(at 100^{o}C). The dielectric constant of this sample remained high (~ 1200) and rather independent with temperature. The microstructure of the cracked surface of Mn doped CCTO samples sintered at 1000^{o}C, appeared dense. The calculated densities of the ceramics were rather high (above 90% of the theoretical density).