CHAPTER 6

THE EFFECT OF In₂O₃ DOPING ON THE DIELECTRIC

PROPERTIES OF CaCu₃Ti₄O₁₂ CERAMICS

6.1. Introduction

CaCu₃Ti₄O (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 [72, 12, 17]. 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 [12]. Change in dielectric constant of CCTO has been wildly related to its microstructure [5]. 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 In doping at B-site of CCTO on the dielectric response have not been investigated. In the present work, the dielectric properties of CCTO ceramics

modified by In_2O_3 have been studied. The electrical properties of the In modified CCTO were reported.

6.2 Experimental

The CaCu₃Ti₄O₁₂ (CCTO) powder was prepared by using solid state synthesis methods. High purity (> 99.9%) CaCO₃ (Riedel-de Haen), TiO₂ (Riedel-de Haen) and CuO (Aldrich) powders were mixed and milled in ethanol using a vibratory mill for 6 h. For the doping study, In₂O₃ powders were added to CCTO at the calcination stage based on the stoichiometry in concentrations of 0.5, 1.0 and 2.0 mol %. Each batch was then calcined in air at 900 °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/cm² into discs, typically 10 mm in diameter and 2 mm in thickness. The discs were sintered in air at 1,100°C for 4 hours with a heating and cooling rate of 5°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 °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).

6.3 Results and discussion

The XRD result for the ceramic samples is shown in Figure 6.1. All the peaks were matched with the standard 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.



(B) Lattice parameter (Å) as a function of In concentration.

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). The lattice constant (Å) as a function of In content is shown in figure 6.1(B).



Figure 6.2 Density and shrinkage as a function of doping concentration

of the samples.

The lattice constant slightly increased as the amount of In_2O_3 increased. This implies that small amount of In ions could go into solid solution with the CCTO lattices. In addition, density and shrinkage slightly increased with the concentration (Figure 6.2), suggesting that the doping oxide slightly promoted the densification.





Fractured surfaces of the CCTO ceramics (undoped and doped 0.5, 1.0, 2.0 mol% In_2O_3) are displayed in Figure 6.3. In_2O_3 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 ~2.7 µm for the 2.0 mol% sample (inset of Figure 6.2). Hence, In_2O_3 doping inhibited grain growth. This result suggested most of the doped oxide still presented out size the lattices. This may cause a segregation of doping oxide and/or forms secondary phases on a very small scale at the grain boundaries which cannot detect by XRD. The segregation phases can prevent grain boundary movement during the processing [75] as a result in the grain growth inhibition.







Figure 6.4 Dielectric constant as a function temperature of the samples: (a) pure CCTO, (b) 0.5 mol% doped CCTO, (c) 1.0 mol% doped CCTO and (d) 2.0 mol% doped CCTO.

The temperature dependences on dielectric constant and loss tangent at various frequencies of the ceramic samples are presented in Figure 6.4 and 6.5, respectively. For the unmodified CCTO, the dielectric constant exhibited a stronger dielectric-frequency dependent while the doped samples showed a weaker dielectric-frequency dependent. It should be noted that at a high frequency, all samples showed a dielectric independent of temperature. The dielectric constant at room temperature and at 1 kHz decreased from 36,300 for the unmodified sample to 24,250 for the 2.0 mol% sample.





pure CCTO, (B) 0.5 mol% doped CCTO, (C) 1.0 mol%

doped CCTO and (D) 2.0 mol% doped CCTO.

The reduction in dielectric constant have been observed for many modified CCTO ceramics [34, 74]. However, the doping improved in the loss tangent performance (Figure 6.5). The loss tangent at room temperature and at 1 kHz decreased from 0.06 for the unmodified sample to 0.05 for the 2 mol% sample while at 500 kHz, it decreased from 0.51 for the unmodified sample to 0.14 for the 2mol% sample. However, the lowest loss tangent was 0.02 at 1 kHz and at ~61 $^{\circ}$ C (inset of Figure 6.5 (D)).





Figure 6.6 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 6.6. The dielectric constant decreased with increasing frequency. For frequencies 100 Hz-10 kHz, however, the loss tangent decreased with increasing the frequency (until 10 kHz), then increased with further frequencies.

Since there was the significant change in microstructure of the samples after doping, hence, the dielectric performance should be related to the characteristic of the grains. In our case, a reason to explain the reduction in dielectric constant may be the decrease in grain size which has been mentioned by many authors [77, 78]. An empirical relation between dielectric constant (at 1 kHz) versus reciprocal grain size of the present samples is plotted in Figure 6.7. With increasing the reciprocal grain size, a linear reduction of the dielectric constant was observed. Furthermore, the lower tangent loss for the doped samples in the present work might be correlated with grain boundary characteristic, i.e. an increase in total resistivity of grain boundaries [79] (which in turn depends on the value of grain boundary resistance of the grains) results in a low loss tangent. However, further investigation work should be attempted to clarify the evidence.



6.4 Conclusions

Dielectric properties of pure CCTO and In 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. The significant change in microstructure of the doped samples suggested that the loss tangent performance should be related with the characteristic of the grain boundary.



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