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Effect of Calcination Temperature on Dielectric Properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ Ceramics

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Abstract

The effect of calcination temperature on the properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramics was studied. CCTO ceramics were prepared using solid state reaction method. The raw materials of CCTO were wet mixed for 24 hours and was dried overnight. CCTO powders were then calcined at three different temperature which is at 900°C, 930°C and 985°C for 12 hours. The calcined powders were compacted at 250 MPa and then were sintered at 1040°C for 10 hours. X-Ray Diffractometer (XRD) analysis showed the formation of CCTO phase and secondary phases of CuO for C900 calcined powder but single phase of CCTO was obtained by C930 and C985 calcined powders. Single phase of CCTO also were seen for all sintered samples. Observation on Scanning Electron Microscopy (SEM) micrographs showed abnormal grain growth or large grain size was seen in C900 sample and finer grain size was observed for C930 and C985 sintered samples. C900 sintered sample obtained the highest dielectric constant (10,462) and the lowest dielectric loss (0.061) measured at 1 MHz.

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1. Introduction

Materials with high dielectric constants and low dielectric loss have attracted a huge interest for technological electronic applications such as capacitors, resonators and filters. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramic was known to have giant dielectric constant ($\epsilon_r \sim 10^4$) at room temperature^{1, 2}. Unfortunately, CCTO cannot be commercialized yet for practical applications due to its high dielectric loss (>0.05 at 1 kHz)^{3, 4}. There are several explanations for the mechanism of the unique dielectric properties of CCTO that have been discussed among researchers⁵⁻⁸ and one of the factors that contributed to the unique dielectric properties of CCTO can be related to the microstructural grains⁸. Most of the researchers claim that giant dielectric constant is interrelated with larger grain size. Therefore, many researchers studied the relationship between the microstructural grains and dielectric properties of CCTO. Besides, the contributions of an extrinsic nature which associated with imperfections in the crystal structure such as microstructural defects, microcracks, grain boundary, porosity and impurities were also counts.

Brizé et al. (2006)⁹ and Mohamed et al. (2013)¹⁰ claimed that the dielectric properties of CCTO are very sensitive to the processing process such as mixing, calcination, shaping and sintering. Many researchers are concentrating on sintering process, because it is important to find the right sintering parameter such as the sintering duration and temperature. However, calcination process also is a very important process. Hutagalung et al. (2007)¹¹ had studied the effect of different calcination time on the properties of CCTO ceramics but no other researchers had focused on the effect of different calcination temperature yet. Calcination helps to produce ceramic powder with excellent sinterability. The shrinkage of the sample during sintering can be affected by calcination temperature. It is because surface area of powders and particle size can differ depending on it. Thus, in order to get high dielectric ceramics, one of the most important step is to optimize the calcination temperature for obtaining a high densification ceramic body. The understanding of this part is very important because it is believed that different calcination temperature can affect the properties of the sintered sample afterwards such as grain size formation. As mentioned earlier, different grain size can influence to the dielectric properties of CCTO. Thus, the studied of calcination temperature is a vital role to improve the dielectric properties of ceramics. Hence, this work focused on the effect of calcination temperature on the dielectric properties of CCTO.

2. Experimental Procedure

CCTO ceramics were prepared by using conventional solid state method. The raw materials of CaCO_3 , CuO and TiO_2 were wet mixed using ethanol for 24 hours and then the mixture was dried overnight in oven. After that, the mixing powders were calcined at three different temperature (900°C, 930°C and 985°C) for 12 hours. The sample was labelled as C900 for CCTO that calcined at 900°C while C930 and C985 were stand for CCTO that calcined at 930°C and 985°C respectively. The mixed powders were compacted into pellets at 250MPa and then the pellets were sintered at 1040°C for 10 hours. All calcined powders and sintered samples were analysed using X-ray Diffraction (XRD) X-ray Diffraction (XRD) (Bruker Advance D8) to identify the phase present. Meanwhile, Field Emission Scanning Electron Microscopy (FESEM) (Zeiss SUPRA 35VP) was used to observe the microstructures and grain growth formation of CCTO. For electrical measurement analysis, the pellets were polished and were coated with silver paint on the both surfaces. Dielectric properties of the sintered samples were measured by using the Impedance Analyzer machine (RF Impedance/Material Analyzer 4291B Hewlett Packard) at frequency 1 MHz.

3. Result and Discussion

Fig. 1 shows the XRD pattern of calcined CCTO powders (C900, C930 and C985). XRD analysis showed the formation of CCTO phase (ICDD no: 01-075-2188) and CuO phase (ICDD no: 03-065-2309) were seen for C900 calcined powder while single phase of CCTO was obtained by C930 and C985 calcined powders. The formation of CuO phase show the C900 calcined powder still has an unreacted raw materials and indicate an incomplete calcination process. It might be caused by the decomposition of CCTO during heating (Hu et al. 2014)¹². Theoretically, the Cu^{2+} cations are reduced at $T \approx 1000^\circ\text{C}$ into Cu^+ and the Cu^+ will reoxidize during the cooling¹³. Subramaniam et al. (2000)¹ also reported the existence of impurity CuO in their CCTO sample as well. However, after sintering process, single phase of CCTO was form for all samples, as shown in Fig. 2.

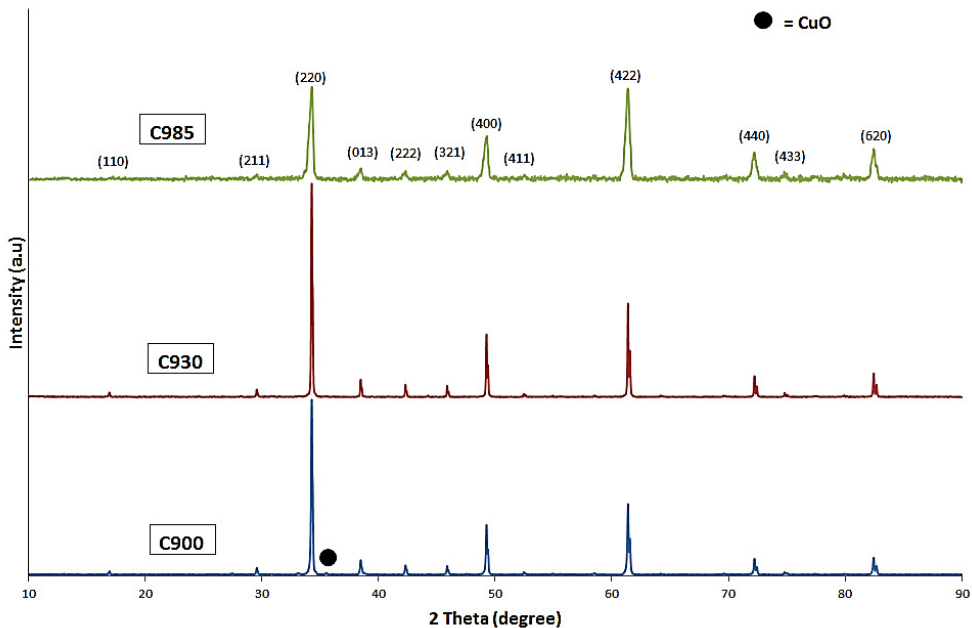


Fig. 1. XRD patterns for CCTO powders that calcined at 900°C, 930°C and 985°C.

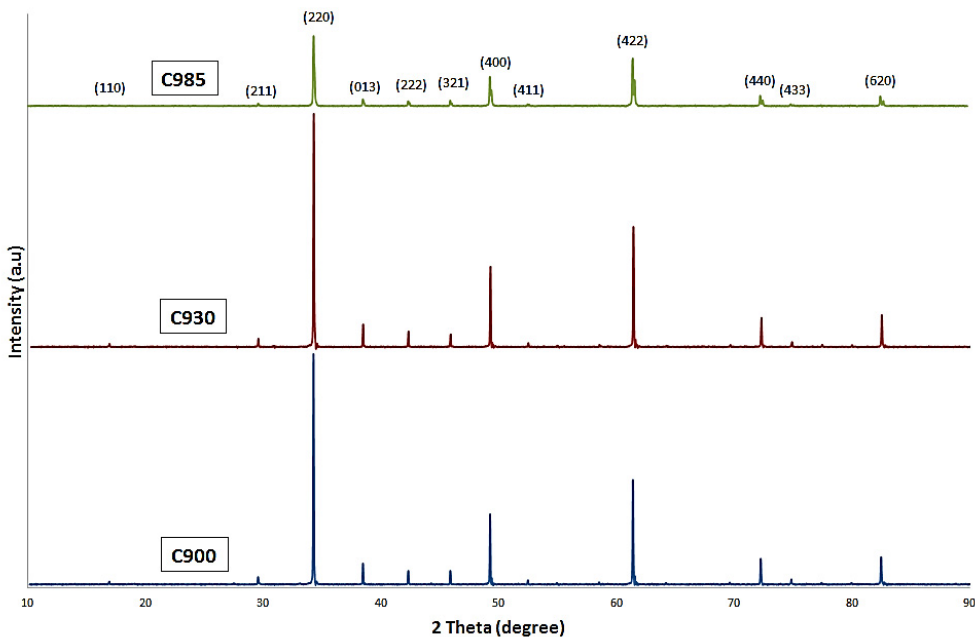


Fig. 2. XRD patterns for CCTO sintered samples with different calcination temperature.

Fig. 3 shows SEM micrographs of C900, C930 and C985 sintered samples. It shows that C900 sample had a large grain size and abnormal grain growth, as shown in Fig. 3(a). The average grain size of C900 is ~27.5 μm. From the microstructure viewpoint, the C900 sintered sample was seen to be the densest, with some solidified

melting CuO phase at grain boundaries. Large grain growth was caused either by CuO or Cu₂O segregates at the grain boundaries of CCTO ceramics¹⁴. Liquid phase of CuO promotes abnormal grain growth and provides an enhanced diffusion path for abnormal grain growth. However, increasing calcination temperature seems to make the grain size of CCTO ceramics becomes finer (Fig. 3 (b, c)) and high porosity were seen for both of the samples. The average grain size of C930 and C985 are ~2.3 μm and ~1.8 μm respectively. This happened might be due to the liquid phase of CuO was not formed after calcination process. Because of that, both of these samples form a finer grain size after sintering process.

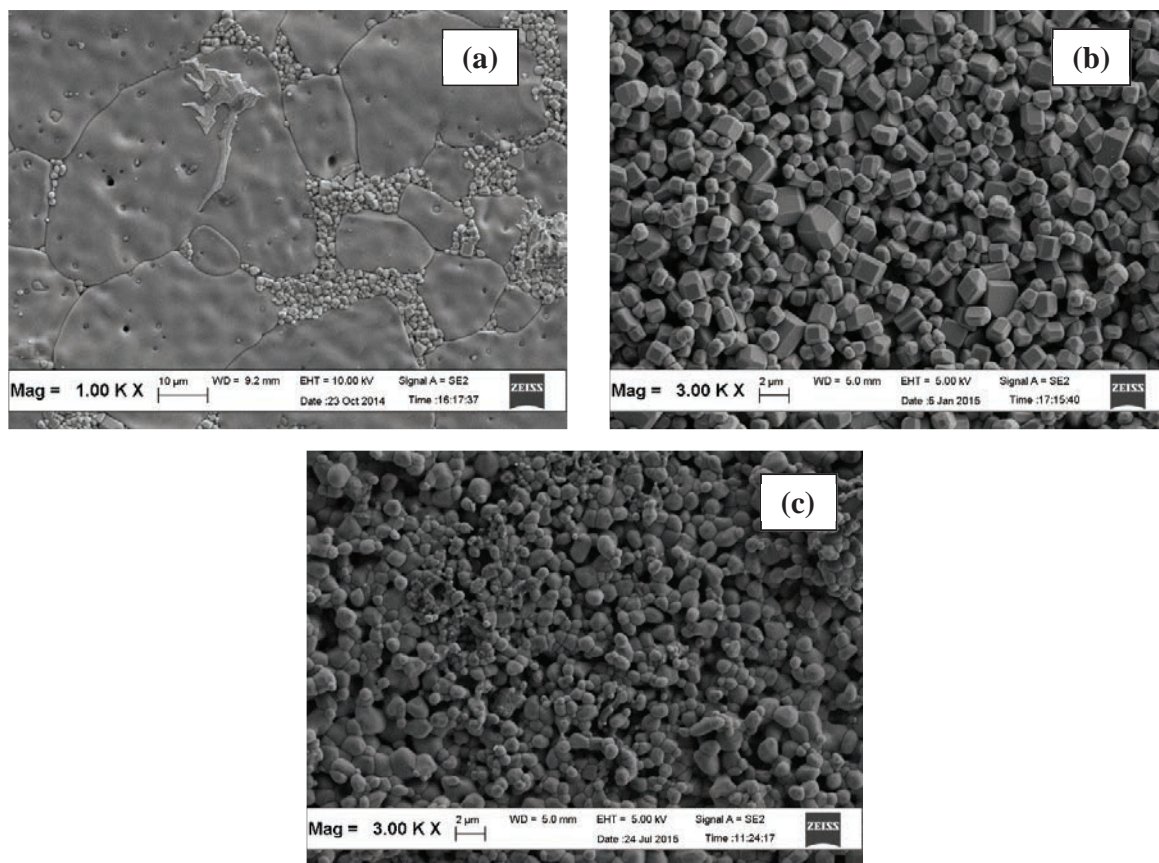


Fig. 3. SEM micrographs of CCTO samples that calcined at (a) 900°C, (b) 930°C and (c) 985°C.

The graph of dielectric constant and dielectric loss of CCTO samples with different calcination temperature was shown in Fig. 4. All of sintered CCTO samples were measured at 1 MHz. From this figure, C900 sample exhibited highest dielectric constant (10,462) compared to the other sample. As stated by the previous researchers, this result can also be correlated to the grain size formation of the sample^{7, 8}. Based on SEM micrographs at Fig. 3, the grain size of CCTO was clearly become finer with increasing calcination temperature. By referring to the equation of Internal Barrier Layer Capacitor (IBLC) model; $\epsilon' = \epsilon_{gb}(t_g/t_{gb})$; where ϵ' is the dielectric constant of sample, ϵ_{gb} is the dielectric constant of the insulating grain boundaries, t_g is the average grain size, and t_{gb} is the average grain boundary thickness, it is clear that the dielectric constant of the CCTO ceramics can be decreased by reducing grain size and/or increasing grain boundary thickness^{7, 15}.

On the other hand, increasing calcination temperature can increase the dielectric loss of CCTO. As seen in Fig. 4, C900 sintered sample obtained the dielectric loss of 0.061 while C985 sintered sample recorded the highest dielectric loss (0.11) which measured at 1 MHz. Based on the IBLC model, the dielectric loss is believed originates

from the conductivity of the CCTO conducting grains and insulating grain boundary, and the conductance of the grain boundary causes the leakage loss¹⁶. Increasing of calcination temperature might reduce grain boundary thickness during sintering. Since grain boundary thickness of CCTO is form by the aggregation of CuO and CuO phase was not detected after calcination process for C930 and C985 calcined powder, thus decrease of grain boundary thickness during sintering could increase the conductance of grain boundary and caused upward trend of dielectric loss. Besides, higher porosity for C930 and C985 (Fig. 3 (b, c)) sintered samples can also contributed to the high dielectric loss. Thus, these results indicate that the properties of CCTO ceramics were also depend on the calcination temperature.

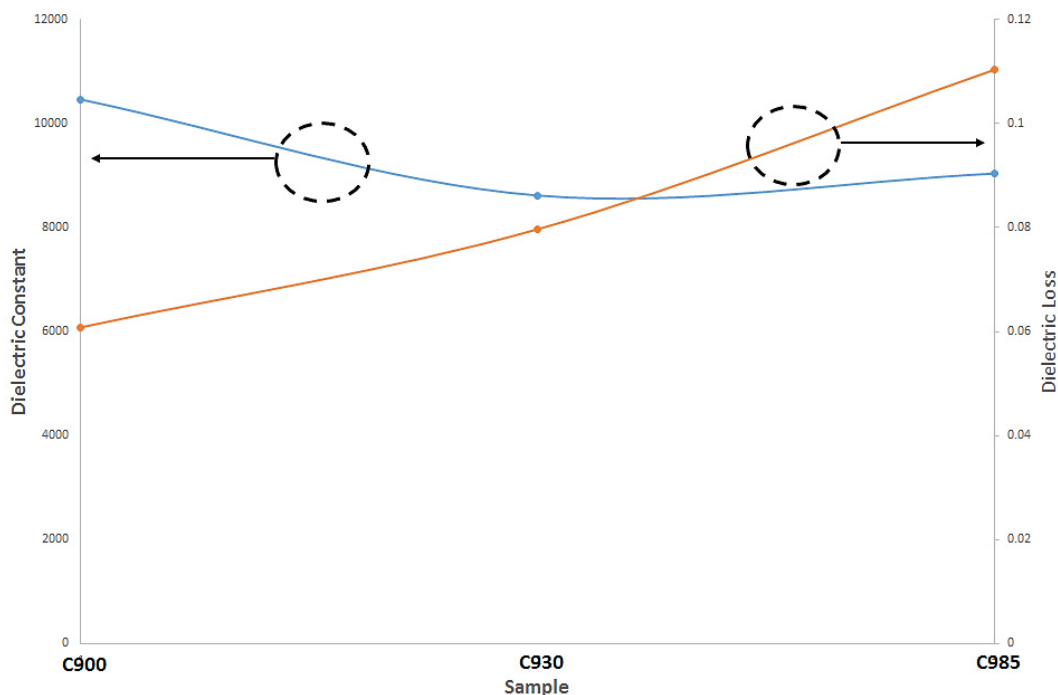


Fig. 4. Dielectric constant and dielectric loss of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics with different calcination temperature measured at frequency 1 MHz.

4. Conclusion

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramics were successfully prepared by using solid state reaction method. Effect of calcination temperature was studied. X-Ray Diffractometer (XRD) analysis showed the formation of CCTO phase and secondary phases of CuO for C900 calcined powder but single phase of CCTO was obtained by C930 and C985 calcined powders. Single phase of CCTO also were seen for all sintered samples. Observation on Scanning Electron Microscopy (SEM) micrographs showed abnormal grain growth was seen in C900 sample and finer grain size was observed for C930 and C985 sintered samples. For dielectric measurement, C900 sintered sample obtained the highest dielectric constant (10,462) and lowest dielectric loss (0.061). Smaller grain size, reduction of grain boundary thickness and higher porosity observed for C930 and C985 samples compared with C900 sample contributed to their low dielectric constant and high dielectric loss.

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