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Effect of Calcination Time on the Microstructure and Dielectric Properties of $CaCu_3Ti_4O_{12}$ using Enhanced Microwave Processing

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Abstract

Calcium copper titanate, $CaCu_3Ti_4O_{12}$ (CCTO) is an electroceramic that belongs to the perovskite structure family. CCTO has received much attention due to its very high dielectric constant. However, it has a high dielectric loss that undesirable in the electronic application. Researchers have studied many methods to overcome the problem thus in this study, the influence of microwave radiation during calcination to the electrical properties was investigated. The synthesis process of CCTO samples was carried out using a solid-state reaction route. The calcination process was conducted at 500℃ with different calcination time using microwave furnace operated at the frequency of 2.45 GHz and assisted with enhanced silicon carbide (SiC)-based susceptor. XRD pattern revealed that the formation of cubic perovskite CCTO was obtained partially after calcination at 500℃ for more than 5 hours, but the single-phase CCTO was not completely formed at this temperature. The SEM microstructure showed grain growth and reduction in porosity and grain boundaries of the pellets with the increase of calcination time. Dielectric properties also increase with the increase of calcination time. The dielectric constants for the CCTO pellets were found to vary from 200 to 2900 in the frequency range of 1 MHz to 10 GHz.

Keywords: CCTO, microwave processing, calcination, phase formation, dielectric properties

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Introduction

Electroceramics have a wide range of growing field that covers magnetic, dielectric, ionically conducting, semiconducting and superconducting ceramics [1]. Calcium copper titanate, $CaCu_3Ti_4O_{12}$ (CCTO) is a perovskite-based centrosymmetric material that has received much focus and attention due to its natural properties of giant dielectric constant (up to 10^5) over a broad temperature range extending from 100 to 600 K [2], [3]. The giant dielectric properties of CCTO is still been questioned till date. Most researchers believe that the extrinsic dielectric constant of CCTO are possibly caused by interfacial polarisations at grain boundaries, or insulating surface layers [4]. CCTO is widely used and become promising material for microelectronic and microwave devices application due to its unique properties. Many researches have been conducted on producing the CCTO using conventional solid-state processing technique [5]–[7]. Calcination is one of the stage from solid-state processing technique where sample is treated with certain heat to have chemical reaction between the material mixture to bond together resulting a new compound. Calcination time is an important parameter of the process in order to study the phase formation after certain time frame. Previous study only discusses on the phase formation at different calcination temperature [7]. However, the conventional heating technique used in producing CCTO is not efficient because requires high temperature and long duration of heat treatment which also led to high production cost [8]. Moreover, CCTO that produced via conventional ceramic processing has a very high dielectric loss which turns it inadequate for electronic application such as a capacitor that tends to store electrical energy instead of loss energy [9], [10]. It appears that dielectric properties of CCTO are very sensitive to processing. Therefore, some researches have been focused on the other methods to synthesise CCTO powder, such as mechanical alloying, polymeric citrate precursor route, microwave synthesis, sol-gel method and several more [11]–[14].

In the late 1950s, the possibility of microwave processing ceramics was discovered and investigated on a limited basis in the 1960s [15]. Microwave heating is a process that generates heat within the materials by exposing it to microwave radiation before heating the entire volume. Microwave synthesis has been suggested as an alternative way to produce CCTO because it is found that this method is able to produce CCTO with high efficiency, high product yield, short duration, energy-saving and high dielectric properties with the low dielectric loss [16]. Hence, in order to enhance microwave synthesis method to become more efficient, a study on the effect of calcination time on the properties of CCTO using enhanced microwave processing was conducted. The enhanced microwave processing method plays a significant role in forming the CCTO faster and with lower temperature compared to the conventional method. Based on a study, the surface morphology shows how the grain growth develop from conventional furnace process compared to microwave sintering process as per Figure 1 below [17]. An enhanced SiC-based susceptor is also used to assist the synthesis of microwave processing. This susceptor is a material that acts as an additive in small concentration, which attenuates microwave energy by absorbing it to improve heating throughout the composite [18]. The SiC-based susceptor used is enhanced from the commercial SiC-based susceptor by adding on clay to upgrade the ability for two-way heating with reduced heat losses from the surface of the material. With the addition of clay, the complex molecules formed lead to the vibration between molecules become more vigorously and hence generate more heat energy [19].

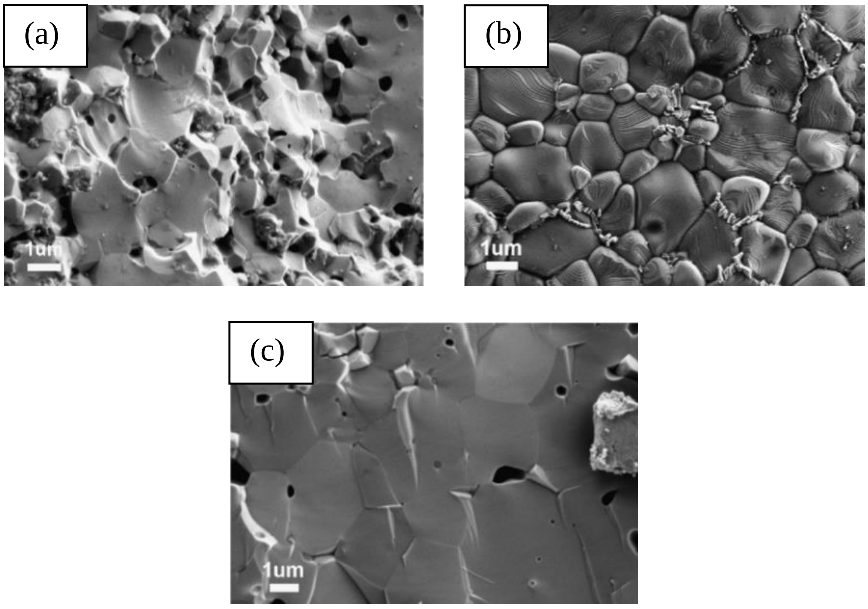

Figure 1: Surface Morphology of FESEM image (fracture) of sintered CCTO pellets (a) at 1000℃/10h using a conventional furnace, (b) at 120 min using microwave, pre-sintered at 1000℃/10h using a conventional furnace, (c) at 120 min using microwave.

Materials and Methods

The CCTO was prepared according to the stoichiometric ratios from reagents of CuO (Aldrich, 99%), TiO_2 (Merck, 99%), and $CaCO_3$ (Aldrich, 99%) powders. The mixing process was conducted by using a milling machine assisted by conventional zirconia ball milling for 24 hours [20]. The ratio between raw materials to zirconia ball milling was 1 to 10. Ethanol was used as a medium for the milling process. The sample powders were placed on top of the enhanced SiC-based susceptor in a crucible to undergo calcination process. The sample powders were calcined in the microwave auto-controller machine (DAWNYX, 2.45 GHz) at 500℃ for the different time (1, 3, 5, 7, and 9 hours). The sample powders were pressed into cylindrical with 5 mm diameter of the mould with the pressure of 300 MPa using a hydraulic hand press machine. Pellets formed were sintered at a fixed temperature of 1040℃ for 10 hours in the conventional furnace.

XRD analysis was performed for calcined powder (microwave processing) and sintered pellets (conventional processing) in order to investigate the phase formation of CCTO at different time by using D2 PHASER X-Ray Diffractometer from Bruker. The XRD analysis was done by using Eva software that can give specific information on the sample results. CCTO pellets that calcined at different time after the sintering process by using conventional processing were characterised using JEOL JSM-IT 100 Scanning Electron Microscope (SEM) to evaluate the microstructure of the CCTO pellets. The Archimedes principle was applied to measure the bulk density and apparent porosity of the CCTO. Dielectric properties were measured by using RF Impedance/Material Analyser 4291B Hewlett Packard machine from frequency 1 MHz to 1 GHz and network analyser from frequency 1 GHz to 10 GHz in ambient temperature to understand the interaction between microwave and materials.

Results and Discussion

The XRD pattern of calcined powder at different microwave irradiation time (1, 3, 5, 7, and 9 hours) at 500℃ is shown in Figure 2. The patterns detected by XRD show the presence of unreacted phases of $CaCO_3$, CuO and TiO_2 phase, which means that the reaction process is incomplete. CCTO phase was only obtained from the sample calcined at 500°C in 5, 7 and 9 hours. It can be observed from the figure that the highest percentage of CCTO is presented in 9 hours of calcination at 500℃. However, the single phase of CCTO is still not completed due to the present of CuO (Tenorite) and TiO_2 (Rutile).

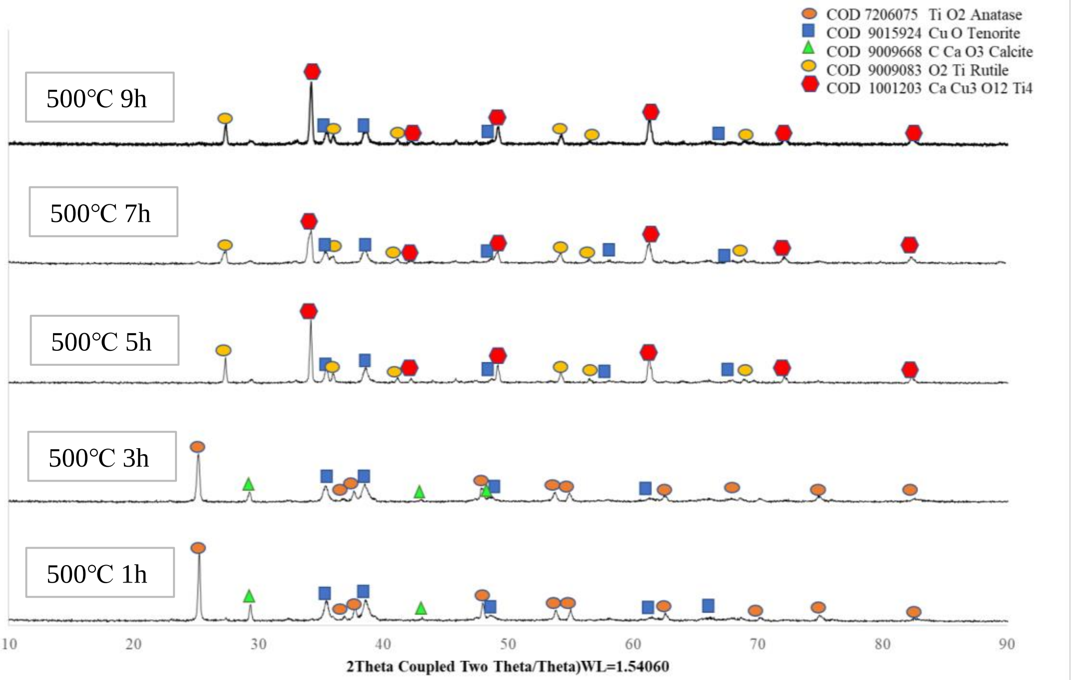

Figure 2: XRD pattern of calcined powder in different microwave irradiation time (1h, 3h, 5h, 7h, and 9h) at 500℃

After the sintering process at 1040℃ for 10 hours, the pellets have undergone XRD analysis. Figure 3 shows the XRD pattern of sintered CCTO pellets at different microwave irradiation time. All of the sintered pellets that calcined at different microwave irradiation time obtained CCTO and TiO_2 (Rutile). There is the highest peak obtained by sintered pellet calcined in 7 hours with a low residue of TiO_2 (Rutile) which is nearly forming single-phase CCTO. As the microwave irradiation time in calcination increases, the CCTO composition in the sintered pellets increase. This good trend is shown for the calcined powder from 1 to 7 hours. The trend shows that the microwave irradiation promotes the production of CCTO composition as time increases. However, there is a drop of CCTO composition in 9 hours since the pellet have already entered secondary phase as it melted, resulting the produced CCTO composition have turned into CuO (tenorite) [12]. To conclude, the highest percentage of CCTO composition with 98wt% is found in the sintered pellets that calcined in 7 hours. However, the CCTO produced is still not completed due to the presence of 2wt% of TiO_2 (Rutile).

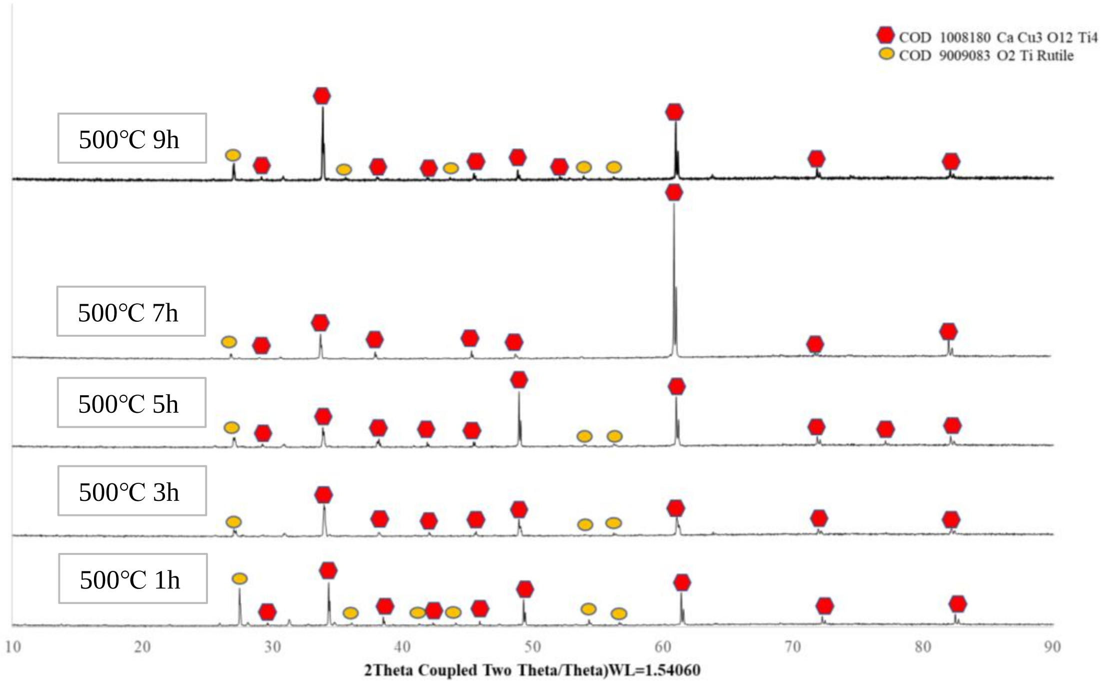

Figure 3: XRD Pattern of sintered CCTO pellets at 1040℃ for 10h of the sample calcined at different microwave irradiation time (1h, 3h, 5h, 7h, and 9h) in 500℃

According to Figure 4, the surface microstructure of sintered CCTO pellets at 1040℃ for 10 hours from calcined powder at different irradiation time was evaluated by using SEM under 1000× magnification which operated in 10 kV. As observed, the amount and grain size of CCTO increases significantly with the increasing of calcination time. The grain growth of CCTO particles and the microstructural densification was promoted by increasing the calcination time as the diffusion process had enough time for CCTO particles to grow for joining together hence reduce the grain boundaries and reduce the porosity of CCTO pellets.

Figure 5 shows the bulk density of sintered CCTO pellets that were calcined at different microwave irradiation time. It shows that the heaviest bulk density of sintered pellets is the sample calcined for 9 hours at 500℃, which is 3.577 g/cm^3 as compared with other parameters. Generally, the bulk density of the sintered CCTO pellets increases with the increasing of calcination time but, there is a decline in the value at 3 hours. Based on Figure 6, the result shows that sintered pellets which calcined for 9 hours at 500℃ have the lowest percentage of apparent porosity with only 13.3%. The percentage of the apparent porosity shows a rapid decrease for the sintered pellets, which calcined for 1 to 5 hours. After 5 hours, the apparent porosity of sintered CCTO pellets becomes almost saturated. It is supported by the previous report studied on the electroceramic systems [2], [21], which agreed that the apparent porosity decreases with the increasing of microwave irradiation time. As a conclusion from Figures 5 and 6, the sintered pellet that calcined for 9 hours can be well said to have a high density with a small size area due to its lowest apparent porosity. The results also prove that the bulk density is increasing as the apparent porosity is successfully decreased with the increasing of microwave irradiation time.

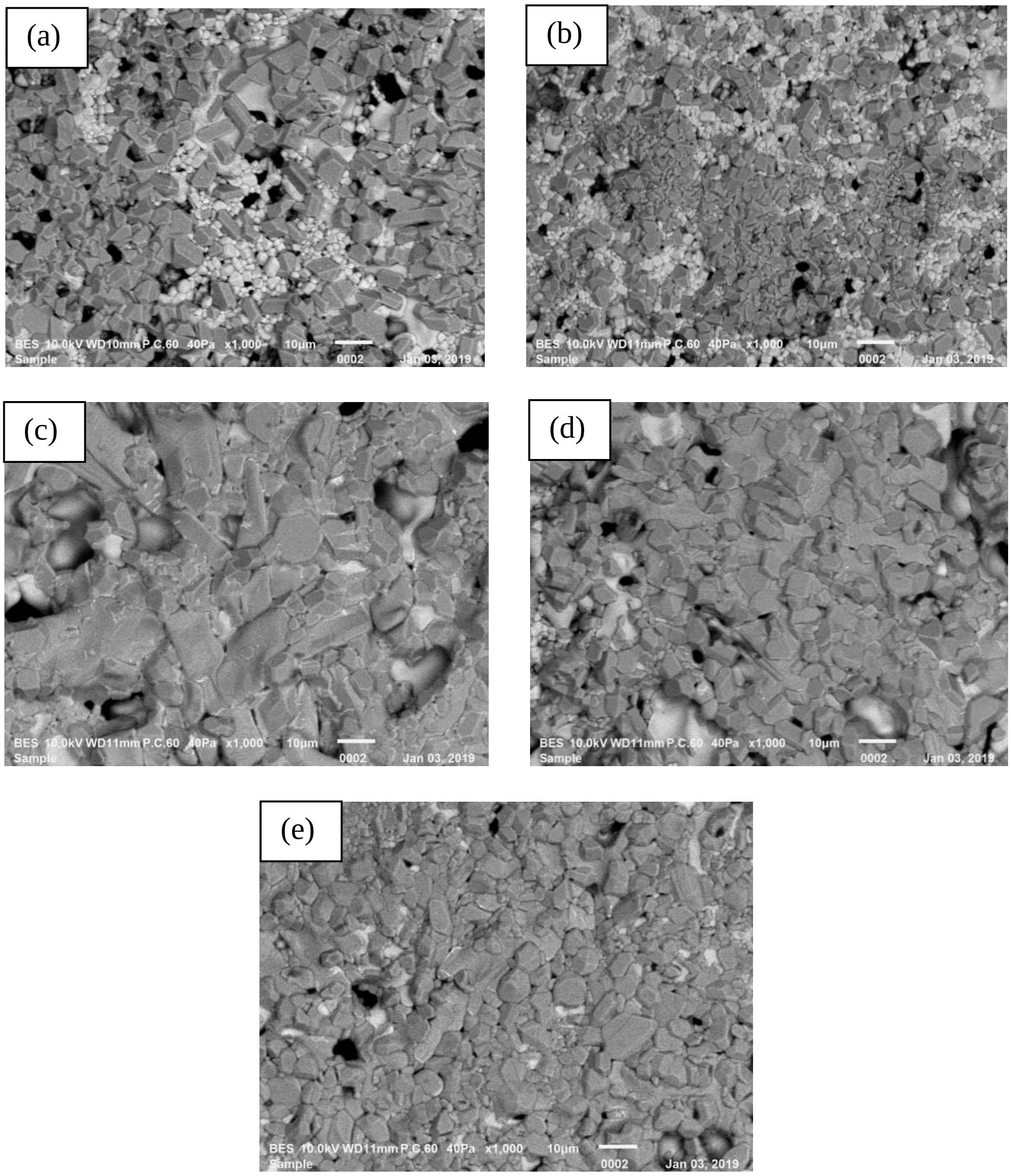

Figure 4: Surface Morphology on sintered CCTO pellets that calcined at different microwave irradiation time which are (a) 1h, (b) 3h, (c) 5h, (d) 7h and (e) 9h

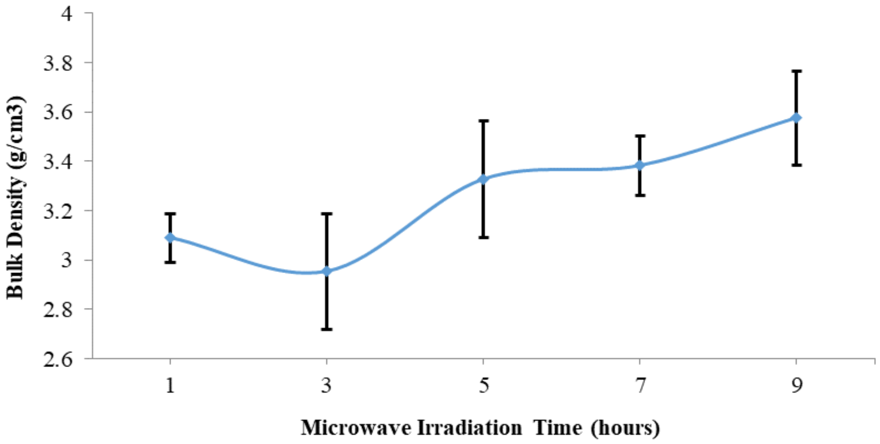

Figure 5: Bulk density of sintered CCTO pellets that calcined in different microwave irradiation time

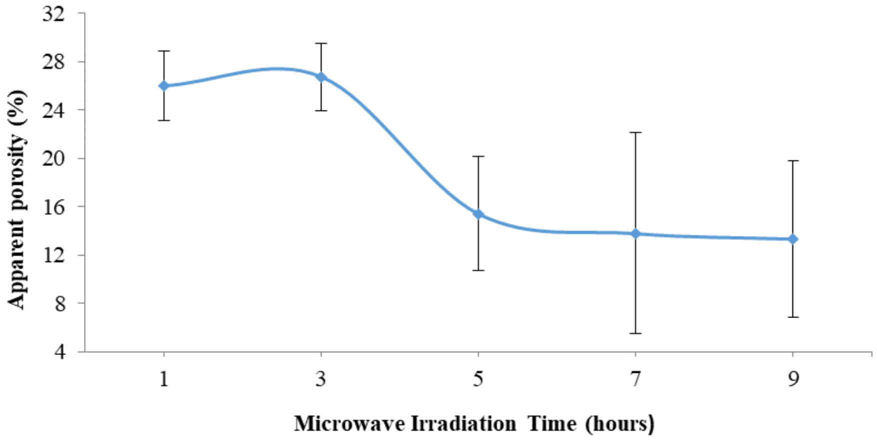

Figure 6: Apparent porosity of sintered CCTO pellets that calcined in different microwave irradiation time

The dielectric properties have been characterised from the frequency range of 1 MHz to 10 GHz by using impedance analyser and network analyser. The dielectric constant plot of sintered CCTO pellets which calcined at different microwave irradiation time is shown in Figure 7. The result shows a significant change of dielectric constant as the function of frequency happens in the range of 1-10 MHz. The dielectric constant is found to increase as the microwave irradiation time for calcination increases except for the sintered pellets that are calcined in 1 hour, which is beyond the trend. In the frequency range of 1-10 MHz, the dielectric constant drop dramatically due to the weakening of space charge polarisation at the critical frequency. Besides that, Figure 8 shows the frequency dependence of dielectric loss of the sintered pellets. In the 1-50 MHz frequency range, there are peaks of all the CCTO sintered pellets. Based on Figures 7 and 8, it can be concluded that the microwave irradiation time (1 MHz) for calcination increases, the dielectric constant and the dielectric loss increase because of the higher dielectric constant sample suffers the higher effect of the weakening of space charge polarisation. The increment of dielectric constant is relevant with the bulk density value, which shows that the increasing microwave irradiation time will produce more CCTO content in a sample.

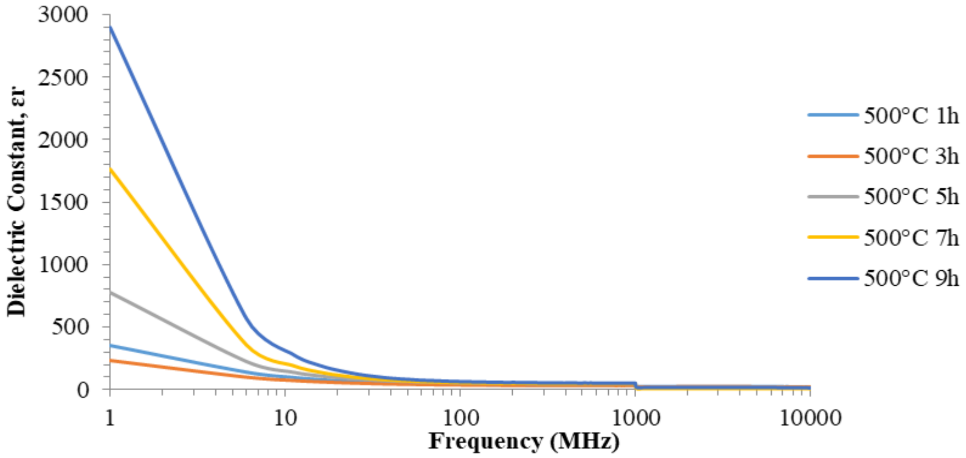

Figure 7: The dielectric constant of sintered CCTO pellets which calcined in different microwave irradiation time at 500°C versus frequency (MHz)

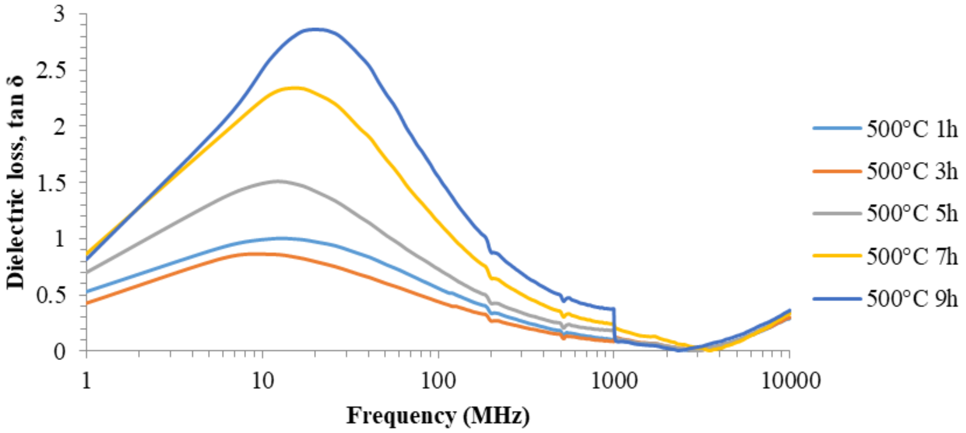

Figure 8: The dielectric loss of sintered CCTO pellets which calcined in different microwave irradiation time at 500°C versus frequency (MHz)

Above all, the enhanced SiC-based susceptor that has been synthesized and commercial SiC-based susceptor were also examined to see their maximum temperature that can be achieved by using a microwave furnace. In Figure 9, it has been shown that the temperature that can be achieved by enhanced SiC-based composite susceptor is higher than commercial SiC susceptor which is 1109ºC. On the other hand, the temperature that can be reached by commercial SiC susceptor is 867ºC. This result had proved that the enhanced SiC-based susceptor can enhance the microwave processing more effectively at the same time duration compared to commercial SiC susceptor.

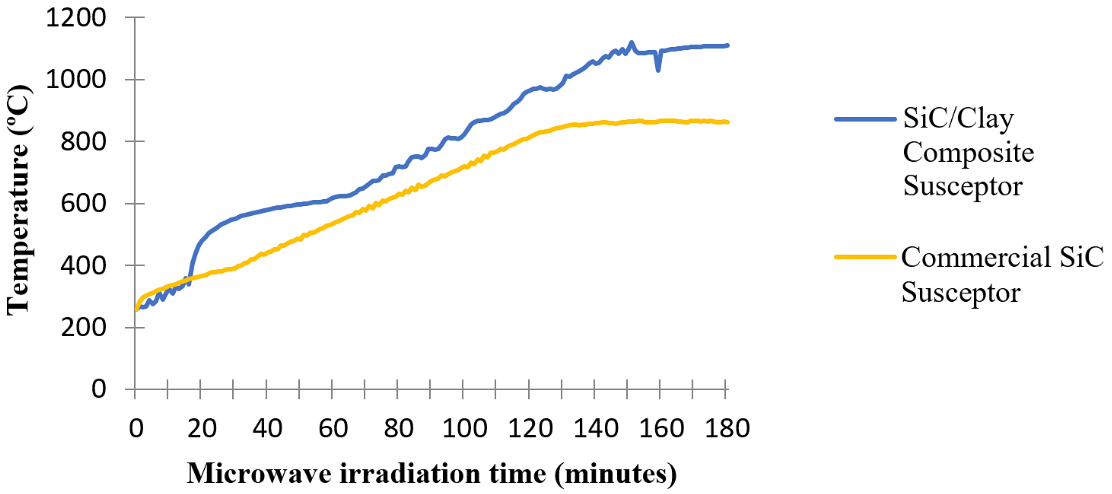

Figure 9: The temperature achieved versus microwave irradiation time

Conclusions

In this research, enhanced microwave processing is used to investigate the effect of calcination time on the properties of CCTO. Based on the XRD analysis, the phase of CCTO was successfully obtained but CCTO did not formed completely and hence, no single-phase CCTO is achieved in the calcination process. The phase formation of CCTO is successfully acquired after sintering for all sintered pellets. The highest percentage of CCTO composition is found in the sintered pellets calcined in 7 hours, which is 98wt%. However, the CCTO is still not completed due to the presence of 2wt% of TiO_2 (Rutile). For the surface morphology of CCTO pellets, as the calcination time and temperature increased, the amount and particle size of CCTO particles also increased, resulting the diffusion process had more time duration to generate energy for grain growth and hence the grain boundaries and porosity can be reduced. The result also has proven that the enhanced SiC-based susceptor can improve the microwave processing more effectively at the same time duration compared to commercial SiC susceptor. For dielectric properties at 1 MHz, the dielectric constant and the dielectric loss increase with the increasing of the microwave irradiation time for calcination, due to the effect of the weakening of space charge polarisation.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare

Compliance with Ethical Standards

The work is compliant with ethical standards

References

[1] N. Setter and R. Waser, “Electroceramic Materials,” *Acta Mater.*, vol. 48, no. 1, pp. 151–178, 2000.

[2] J. J. Mohamed, S. D. Hutagalung, and Z. A. Ahmad, “Influence of sintering parameters on melting CuO phase in CaCu3Ti4O12,” *J. King Saud Univ. - Eng. Sci.*, vol. 25, no. 1, pp. 35–39, 2013.

[3] M. A. Subramanian, D. Li, N. Duan, B. A. Reisner, and A. W. Sleight, “High Dielectric Constant in ACu3Ti4O12and ACu3Ti3FeO12phases,” *J. Solid State Chem.*, vol. 151, no. 2, pp. 323–325, 2000.

[4] W. X. Yuan, S. K. Hark, H. Y. Xu, and W. N. Mei, “Investigation on the growth of CaCu 3Ti 4O 12 thin film and the origins of its dielectric relaxations,” *Solid State Sci.*, vol. 14, no. 1, pp. 35–39, 2012.

[5] R. Löhnert, R. Schmidt, and J. Töpfer, “Effect of Sintering Conditions on Microstructure and Dielectric Properties of CaCu3Ti4O12 (CCTO) Ceramics,” *J. Electroceramics*, vol. 34, no. 4, pp. 241–248, 2015.

[6] P. Liu, Y. Lai, Y. Zeng, S. Wu, Z. Huang, and J. Han, “Influence of Sintering Conditions on Microstructure and Electrical Properties of CaCu3Ti4O12 (CCTO) Ceramics,” *J. Alloys Compd.*, vol. 650, pp. 59–64, 2015.

[7] S. A. Karim, M. A. Sulaiman, M. N. Masri, Z. A. Ahmad, and M. F. Ain, “The dielectric properties of CaCu3Ti4O12 at various calcination temperatures,” *Mater. Sci. Forum*, vol. 888 MSF, pp. 117–120, 2017.

[8] S. Kumar, N. Ahlawat, and N. Ahlawat, “Microwave sintering time optimization to boost structural and electrical properties in BaTiO3 ceramics,” *J. Integr. Sci. Technol.*, vol. 4, no. 1, pp. 10–16, 2016.

[9] B. A. Bender and M. J. Pan, “The effect of processing on the giant dielectric properties of CaCu 3Ti4O12,” *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, vol. 117, no. 3, pp. 339–347, 2005.

[10] M. Oghbaei and O. Mirzaee, “Microwave versus conventional sintering: A review of fundamentals, advantages and applications,” *J. Alloys Compd.*, vol. 494, no. 1–2, pp. 175–189, 2010.

[11] J. Zhao, J. Liu, and G. Ma, “Preparation, Characterization and Dielectric Properties of CaCu3Ti4O12 Ceramics,” *Ceram. Int.*, vol. 38, no. 2, pp. 1221–1225, 2012.

[12] S. D. Hutagalung, L. Y. Ooi, and Z. A. Ahmad, “Improvement in dielectric properties of Zn-doped CaCu3Ti4O12 electroceramics prepared by modified mechanical alloying technique,” *J. Alloys Compd.*, vol. 476, no. 1–2, pp. 477–481, 2009.

[13] P. Jha, P. Arora, and A. K. Ganguli, “Polymeric Citrate Precursor Route to the Synthesis of the High Dielectric Constant Oxide, CaCu3Ti4O12,” *Mater. Lett.*, vol. 57, no. 16–17, pp. 2443–2446, 2003.

[14] P. Thomas, L. N. Sathapathy, K. Dwarakanath, and K. B. R. Varma, “Microwave synthesis and sintering characteristics of CaCu 3 Ti 4 O 12,” *Bull. Mater. Sci.*, vol. 30,

no. 6, pp. 0567–0570, 2007.

[15] S. Wang, *Microwave Processing*, no. Reynolds 1989. 2012.

[16] H. Yu, H. Liu, D. Luo, and M. Cao, “Microwave Synthesis of High Dielectric Constant CaCu3Ti4O12,” *J. Mater. Process. Technol.*, vol. 208, no. 1–3, pp. 145–148, 2008.

[17] S. D. Hutagalung, M. I. M. Ibrahim, and Z. A. Ahmad, “Microwave assisted sintering of CaCu3Ti4O12,” *Ceram. Int.*, vol. 34, no. 4, pp. 939–942, 2008.

[18] T. Bhattacharya, M., & Basak, “A review on the susceptor assisted microwave processing of materials,” *Energy*, vol. 97, pp. 306–338, 2016.

[19] S. J. Park and M. K. Seo, “Types of composites,” *Interface Sci. Technol. Elsevier*, vol. 18, pp. 501–629, 2011.

[20] N. Anadin, “Effect of Zinc Doping on Electrical Properties of CaCu3Ti4O12 Produced Using Conventional and Microwave Techniques,” Universiti Malaysia Kelantan, 2018.

[21] V. Brizé *et al.*, “Grain size effects on the dielectric constant of CaCu3Ti4O12 ceramics,” *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, vol. 129, no. 1–3, pp. 135–138, 2006.