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Zn-Doped Calcium Copper Titanate Synthesis via Microwave-Assisted Technique

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ABSTRACT

Electroceramic material has become significant in the recent development of electronic parts such as capacitors, resonators, and sensors. The previous study on calcium copper titanate ($CaCu_3Ti_4O_{12}$, CCTO) showed that CCTO exhibits a colossal dielectric constant, up to 10^5 for bulk materials using a conventional synthesis route (calcine and sinter at 900 - 1040°C for 9 - 12 hours). The high firing temperature and longer reaction time were undesirable because they would increase production costs and be time-consuming. Alternately, research findings on doping with donor or acceptor elements were proven to be an effective technique for improving dielectric properties. Thus, the Zn-doping (Zn= 0, 1, and 3 mol%) method increased the dielectric constant in CCTO. The study successfully synthesized Zn-doped CCTO at 700°C with a soaking time of 40 minutes using a microwave-assisted technique (calcined and sintered). Then, the samples were characterized using XRD and an impedance analyzer. The CCTO crystal formation was examined through an XRD pattern, and semi-quantitative analysis indicated that 1 mol% of Zn-doped recorded optimum formation reaction after calcining (56.5 wt%) and as-sinter (70.3 wt%). However, despite the low formation of CCTO crystal structure in 3 mol% of Zn-doped (34.9 wt%), it has the highest dielectric constant, and the dielectric loss was reduced at high frequency.

Keywords: Zn-doping; CCTO; Microwave-assisted technique; Dielectric properties

1. Introduction

Ceramics include such a vast array of materials that a concise definition is almost impossible. However, a workable definition of ceramics is a refractory, inorganic, and nonmetallic material. Ceramics consist of two types: traditional and advanced. Traditional ceramics include clay products, quartz sand, cement, and silicate glass, while advanced ceramics consist of nitride (Si_3N_4) [1], carbides (SiC) [2], pure oxides (Al_2O_3) [3], non-silicate glasses and many others. Ceramics presents many advantages compared to other materials, such as being mechanically harder and stiffer than metal. Nevertheless, it is also corrosion-free; raw materials are abundant and inexpensive. However, it has a high melting point and requires high-temperature processing.

A part of ceramic is electroceramic, an advanced material used for electrical properties. Instead of good mechanical, chemical stability, thermal, and optical, electroceramic is also well utilized for electrical and magnetic properties. They have become essential in the recent development of equipment and machines. Among advanced ceramics, electroceramic covers dielectric ceramics, ferrite ceramics, garnet (ferromagnets), and piezoelectric ceramics. The electroceramic can improve application technology and devices. This growing field consists of many magnetic, dielectric, ionically conducting, superconducting, and semiconducting areas. It is known that some ceramic compounds with perovskite structures have been found to have fascinating dielectric properties. In particular, one of the members, $CaCu_3Ti_4O_{12}$ (CCTO), is the latest study to review the origin of the so-called colossal permittivity [4].

CCTO is an electroceramic compound that attracted much attention due to its high dielectric constant (up to 10^5) over a broad temperature range extending from -173.15 to 326.85℃ [5,6]. CCTO is a promising material with unique properties for microelectronic applications [7]. Most CCTO research has been implemented on bulk materials (ceramic or single crystal) and focused on identifying the mechanism responsible for the unusual CCTO properties. The nothingness of any unusual lattice parameter changes across a temperature of -173.15℃, below which an incredible change of the dielectric constant occurs, shows that a structural phase transition, which generally brings to such gradual changes of properties, does not occur in CCTO in the temperature range of interest. It has been proposed that the high dielectric constant is due to an off-center displacement of Ti-ions, producing a dipole moment with a strongly temperature-dependent scattering rate. Based on a series of isostructural materials compared to CCTO, the microstructural of ceramic samples was also emphasized as a possible source of the high dielectric constant [8].

2. Materials and Methods

Firstly, the raw materials of CCTO were prepared: ZnO (R&M, 99%) and $CaCO_3$ (Adrrich, 99%). CuO (Adrich, 99%) and TiO_2 (Merck, 99%) powders and weight according to the stoichiometric ratio ($Ca_{1-x}ZnxCu_3Ti_4O_{12}$), which x = 0, 1, 3, 5 and 10 mol%. Then, the raw material precursors were mixed and placed on a susceptor crucible. The crucible was put inside a domestic microwave with an irradiation time device (40 minutes). Calcined powder was characterized for phase formation and was pressed to the disc-shaped pellet for sintering. The pellets were sintered again using the same microwave furnace assisted with a susceptor crucible at the temperature of 700℃ for 40 minutes in the air and then analyzed for phase formation using Bruker D2 Phase X-ray Diffractometer. The sample tested the dielectric properties using RF Impedance/Material Analyzer 4291B Hewlett Packard at 1 MHz to 1 GHz.

3. Results and Discussion

Fig. 1 shows the x-ray diffraction (XRD) analysis of calcined powder CCTO using a microwave technique at 700ºC for 40 minutes. It proved the formation of CCTO structure because of some of the peak matches with the Crystallography Open Database (COD). The XRD pattern also shows the CCTO phase with its unreacted raw material. The raw materials phase is the same as the original before calcination except for TiO_2. CCTO does not completely form due to insufficient time where the particle needs time to diffuse. Diffusion will allow reaction between raw materials.

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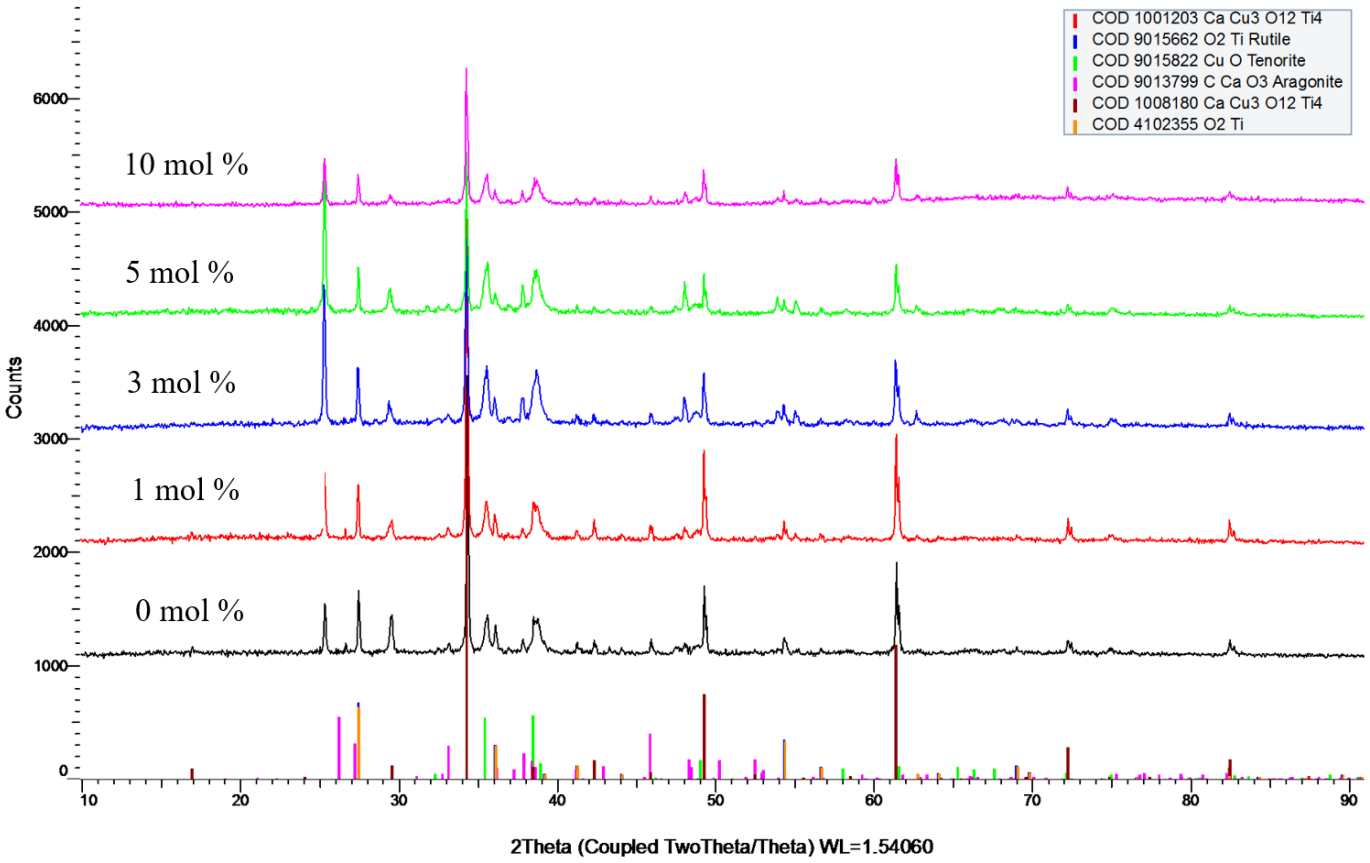

Fig. 1: XRD Pattern of samples after calcination process using microwave technique

A semiquantitative analysis was carried out to extend the understanding of phase formation. Fig. 2 illustrates the phase fraction for all peaks in the XRD analysis of calcined CCTO at the microwave high-power mode. The results indicate that the calcination process using a domestic microwave with a susceptor crucible effectively produced the CCTO. These amounts were 39.73, 56.6, 30.9, 32.1, and 42.2 wt% for samples with 0, 1, 3, 5, and 10 mol% Zn-doped CCTO, respectively [9]. Among the samples, the highest weight percentage of CCTO is 56.5 wt% from the sample with 1 mol% of Zn. CCTO reaction is still incomplete due to the existence of TiO_2, CuO, and $CaCO_3$ [10]. It is suggested that a longer calcination duration of more than 40 minutes and at higher temperatures increase the CCTO formation.

Figures 3 and 4 illustrate the XRD diffraction pattern and phase fraction following sintering using the same microwave at 700°C for 40 minutes. The results indicate that there is no substantial increase in the CCTO phase in all samples, which show values of 55.3%, 70.3%, 34.9%, 27.5%, and 44 wt%, respectively. Notably, the highest CCTO formation was observed in the sample with 1 mol% of Zn, reaching 70.3 wt%, compared to 56.5 wt% after calcination.

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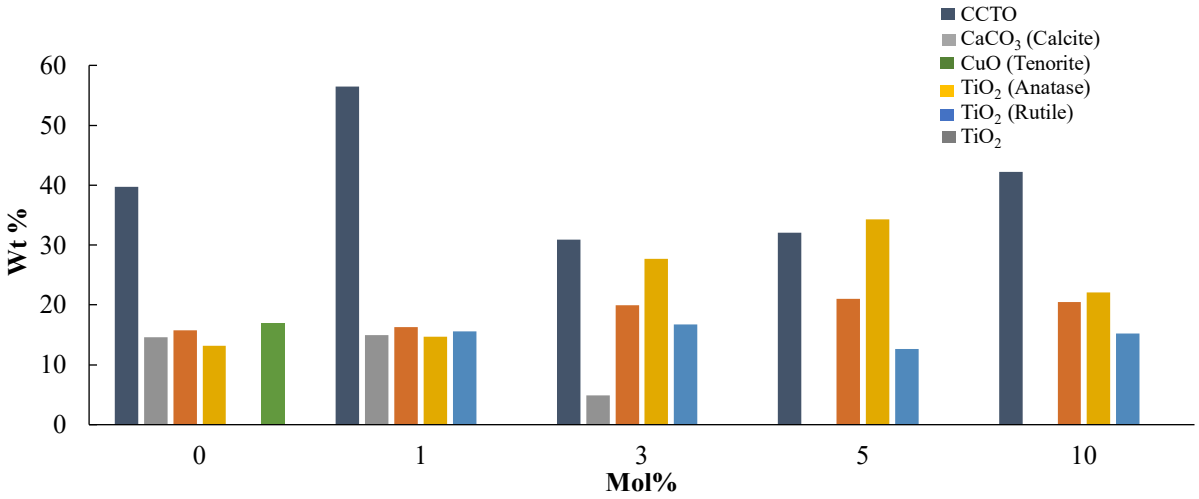

Fig. 2: Phase fraction of different mol % of zinc using semi-quantitative analysis after calcination using microwave technique.

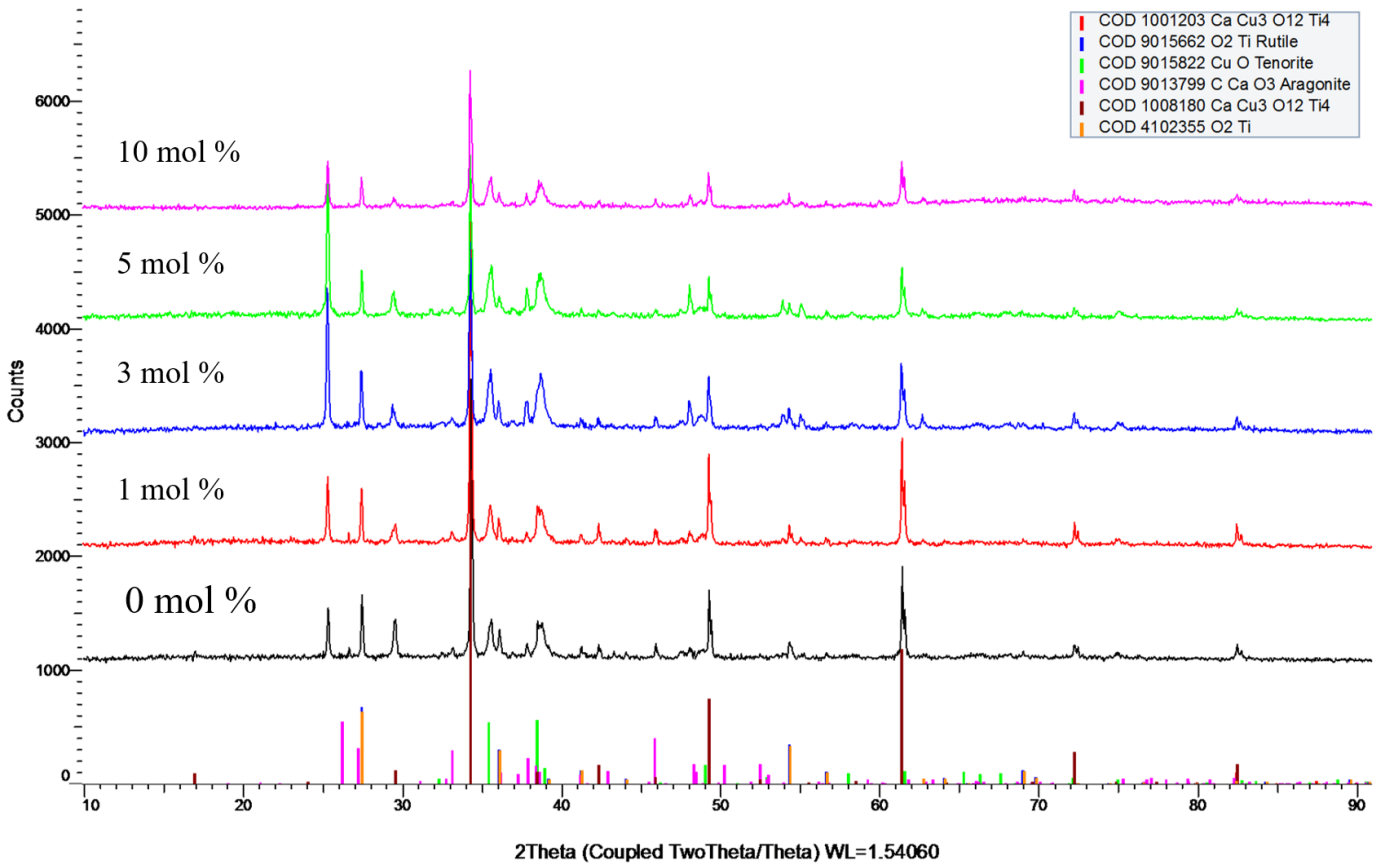

Fig. 3: XRD pattern as-sintered using microwave processing

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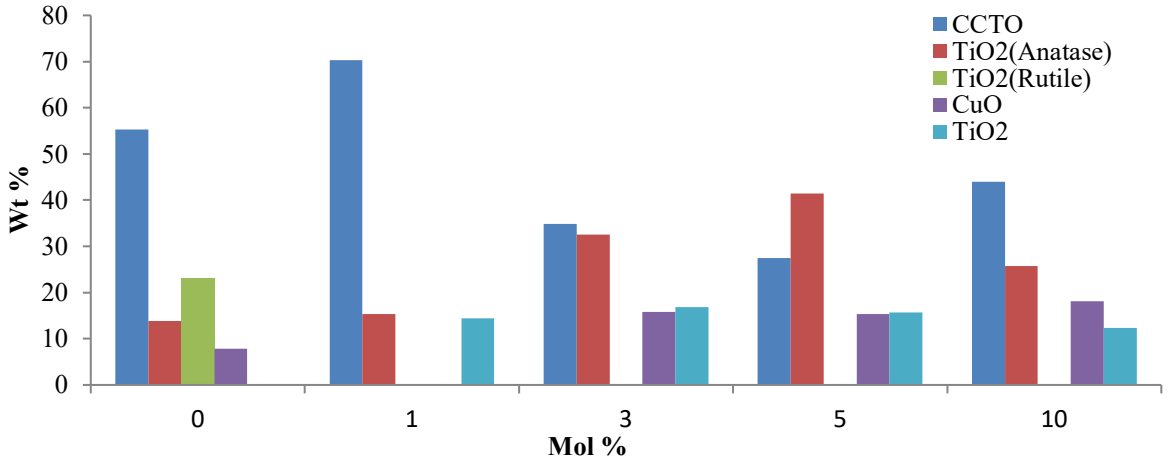

Fig. 4: Phase Fraction of different mol % of zinc using semi-quantitative analysis as-sintered using microwave technique.

Fig. 5 and Fig. 6 show the dielectric constant and dielectric loss of as-sintered CCTO pellets using microwave processing at the frequency of 1 MHz to 1 GHz. The increasing amount of zinc improves the dielectric constant of CCTO material. Samples of 0 and 1 mol % Zn show a stable trend across the frequency range, which are 28.7 – 24.1 for 0 mol% and 39.8 to 26.87 for 1 mol% Zn. However, the dielectric loss gradually decreases at a frequency of 3 mol% of Zn-doped. As observed, the Zn helps to reduce dielectric loss even though the concentration of CCTO was lowered compared to the undoped and 1 mol%; a similar report has been recorded by Juhairi et al. [11] using feldspar.

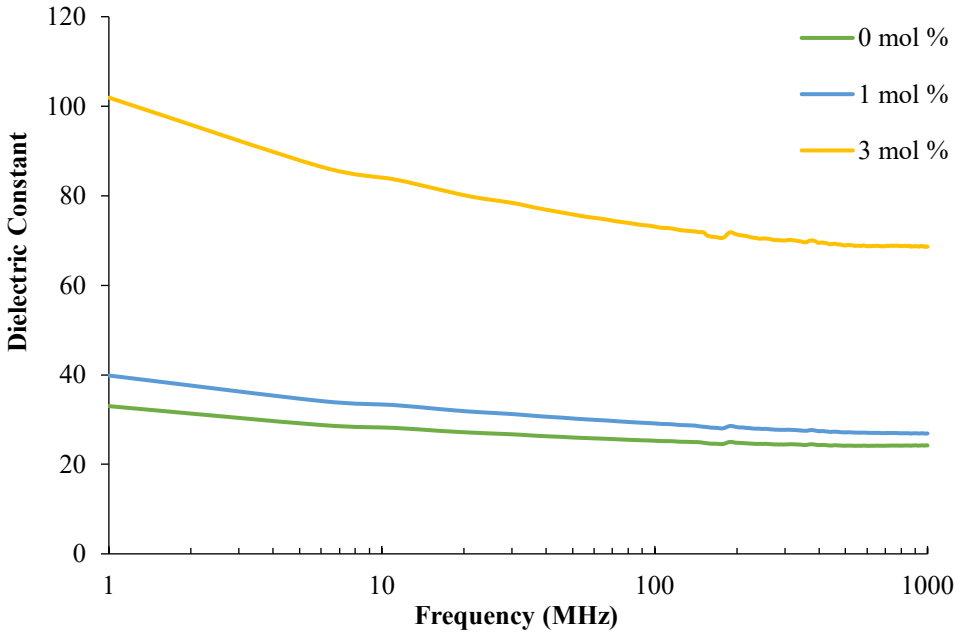

Fig. 5: Dielectric constant of sintered CCTO pellet using microwave technique.

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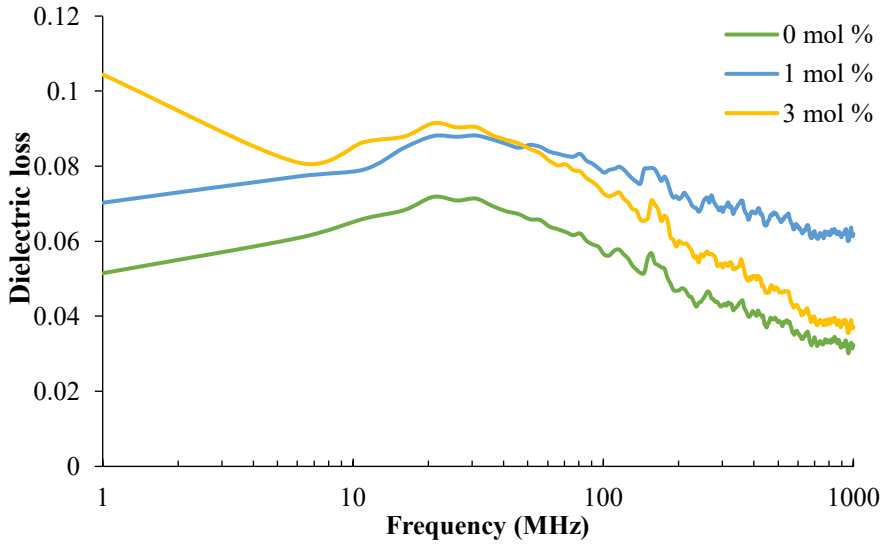

Fig. 6: Dielectric loss of sintered CCTO pellet using microwave technique.

4. Conclusion

The study successfully synthesized Zn-doped CCTO at 700°C with a soaking time of 40 minutes using a microwave-assisted technique for the calcination process. Through an XRD pattern, 1 mol% of Zn-doped CCTO recorded the highest CCTO formation (56.5 wt%) after the calcination process and as-sintered pellets (70.3 wt%). The increasing amount of zinc improves the dielectric constant of CCTO.

Acknowledgements

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