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Improved Densification and Dielectric properties of ZBS-doped $CaCu_3Ti_4O_{12}$ Electroceramics

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ABSTRACT. Analysis and experimental was performed on ZBS-doped $CaCu_3Ti_4O_{12}$to investigate their electrical properties. The pellet samples were prepared via solid-state reaction method. Archimedes principle was used to examine the effect of glass dopant on the densification of CCTO. The density and dielectric properties of ZBS doped CCTO (0, 1, 3 and 7 mol%) sintered at 1040°C show a relative density of ~ 96%, a high dielectric constant of ~ 3000, and a dielectric loss of ~ 1.0.

Keywords: *Solid state reaction, Electrical properties, Glass material;*

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1. INTRODUCTION

Calcium Copper Titanate (CCTO) is a potential candidate used in microelectronic applications (capacitor, filters and resonator) due to its giant relative dielectric constant (ε_r ~ 12 000 at 1 kHz) [1]. Higher ε_r value means more charges can be stored and smaller devices can be fabricated. The relative dielectric constant of CCTO has been reported to be highly dependent on the processing conditions. The solid-state reaction technique is able to produce single phase CCTO but this process usually required a high sintering temperature (≥ 1100 °C) for tedious duration (> 12hours) and dielectric loss (tan δ) obtained is too high for to be used in a commercial microelectronic applications [2]. Mu et al. [3] reported that the typical tan δ value for CCTO ceramics is about 0.1 at 1 kHz in room temperature. Besides, Rahman et al. [4] also stated that CCTO is suffering from a high dielectric loss (0.2-1.0) which prevents its potential applications to be commercialized.

The dielectric loss phenomena happen due to the rotation of the atoms in an alternating electric field. The rotation of a dipole in a material is like a small ball rotating in a viscous fluid. Under an external force which is produced by electric field, it tends to change from its original equilibrium state to a new equilibrium state. This process is generally referred to the relaxation process. Many researchers have proposed a ways to reduce dielectric loss and one of the solutions is by implied the possible doping to modify the CCTO compositions such as SiO_2-doped CCTO, Fe- and Nb-doped CCTO, Cr_2O_3-doped CCTO, $CaTiO_3$ doped CCTO, ZrO_2 doped CCTO.

However for this research, the goal is to produce CCTO ceramic with excellent dielectric properties include of high dielectric constant, high energy density and low dielectric loss. Therefore glass ceramic composite material has been proposed since glassyphases have high electrical resistance and low dielectric loss, so that the formation of this kind of phases, surrounding grains, could assist in the lowering of dielectric loss and in improving the overall dielectric properties of

CCTO Glass ceramic materials are polycrystalline materials that can prepare by controlled the crystallization of glasses where it consist of crystal and glass phase. Glass ceramic was prepared by first obtaining a glass matrix by melt casting and then precipitating a crystal phase in the glass matrix during subsequent heat treatment [5]. High energy density capacitor fabricated by glass ceramic materials can store more than ten times energy per unit volume than the common capacitor.

The combination of high dielectric electroceramic materials and high breakdown strength of glass materials is hope can create high energy density capacitors. Based on our research review, there are some reports about the effect of addition of glass materials or glass formers into the CCTO [6], but there is no systematic study on the densification and dielectric properties with ZBS (ZnO-B_2O_3-SiO_2) glass doped CCTO ceramics. Therefore, in this research ZBS glass were introduced not onlyto promote densification up to 96% but also increased the dielectric properties (high ε_r and low tanδ).

2. MATERIALS AND METHODS

The ZBS glass was prepared via wet-ball-mixing from high-purity starting materials. The mixture was dried in an oven and melted in alumina crucible using glass melting furnace (Lenton EHF 1800) at 1450 ^oC for 2 hours. The molten glass was manually poured into distilled water and the glass frits obtained were ball-milled to form a fine glass powders. Meanwhile, CCTO powder was prepared by solid-state reaction method using high purity starting raw materials of $CaCO_3$, CuO and TiO_2 powders. The mixture powders were wet-mixed with ethanol for 24 hours and dried-overnight in the oven. The dried-mixtures were calcined at 900 °C for 12 hours. Subsequently, the glass powder was mixed with CCTO's calcined powder for different composition ratios as (x)ZBS + (1-x)CCTO, where x = 0, 0.01, 0.03 and 0.07 using zirconia balls media for 24 hours before pelletized. The samples were coded according to the ZBS doping concentration as Z0, Z1, Z3 and Z7, respectively. Then, green body was sintered at 1040 ^oC for 10 hours in air. The density of samples was determined using Archimedes principle method. The dielectric properties were measured using the Impedance Analyzer machine (RF Impedance/Material Analyzer 4291B Hewlett Packard) over a broad frequency range of 1 MHz to 1 GHz.

3. RESULTS AND DISCUSSION

Fig. 1shows the relative density of the CCTO ceramics with different of ZBS addition. The Z1 sample was the densest with highest relative density (~ 96%) compared to pure CCTO (~ 94%). This result indicated that ZBS addition can help to improve the densification of the CCTO ceramics and enhance material transport rate during the sintering process. Z1 sample ceramics possesses superior wetting characteristic on the surface of CCTO ceramic and it helps to fill up the closed pores inside the ceramic body and improve the density of the sample. Hsiang et al. [7] had also stated that ZBS glass can improve the densification of $BaTiO_3$ ceramic sample. However, Z7 sample did not result in high densification. This result may be explained by the formation of secondary phase through interaction between CCTO and glasses, which consumed large amount of glasses, added and resulted in the insufficient amount of liquid phase. Theoretical density value of CCTO is 5.07gcm^{-3}, as reported by Moussa and Kennedy [8].

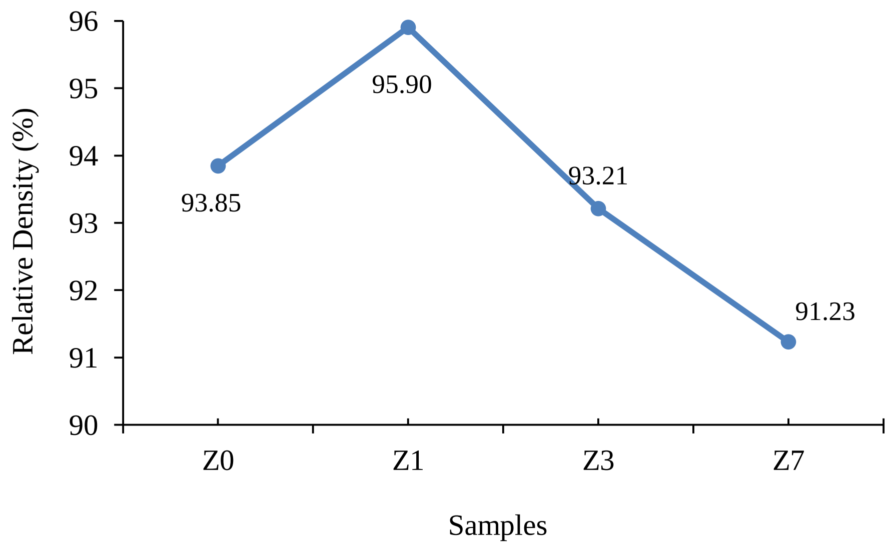

Fig. 1 Relative density of the CCTO ceramics with different of ZBS addition

Fig.2 shows the SEM micrograph of the ZBS-doped CCTO samples. TheZ1 sample shows the average grain size of 5.43 μm. It can be stated that a small quantity of glass additive can reduce a grain size. Each of the samples shows almost the same grain size. This proves the presence of glassy phase can help in obtaining a homogenous microstructure. Increasing the glass content can reduce the average grain size with Z0(5.65 μm)> Z1(5.33 μm)>Z3(4.83 μm)>Z7(2.19 μm). The Z1 samples has less micro-pores compared to undoped CCTO (Z0), which can be attributed that the pores has been filled by the glass phase provided by the ZBS molten glass during sintering process. Previous researchers investigated that there is a fast grain growth at higher ZBS glass amount. A fast grain growth will reduce the average grain size, and then reduce the relative density. Too much ZBS glass content prevent an excessively of the grain growth [9]. This effect can be seen for the Z7 samples.

The effects of the glass additions on the dielectric constant of CCTO ceramics are shown in Fig. 3. The dielectric properties obviously depend on ZBS glass composition. The porosity and grain size played dominant roles in determining the magnitudes of dielectric behavior. The results shows that, the dielectric constant value for Z1 sample gives highest value up to ~ 3000 compared to other sample. The drastic changes in dielectric constant happen when grain boundaries at cooling stage re-oxide faster than the interior of the grains which prevents degradation of the enhanced conductivity of the bulk grains. Fast diffusion on grain boundary has made it become insulative leading to the formation of the higher dielectric constant.

The improvement in dielectric properties was also correlated to the relative density value of the pellets as shown in Fig. 1. In other words, higher densification may play a role in enhancing the value of dielectric constant. Besides, a higher density for a ceramic means there are more dipoles in a unit volume, so the sample with a higher density has a larger dielectric constant value. The improvements in densification are related to the step of nucleation theory where the reason for the development of discontinuous grain growth. Based on the theory, the discontinuous grain growth can occur by the step growth mechanism where the flat and faceted grain boundaries are expected to have singular structures which promoted abnormal grain growth.

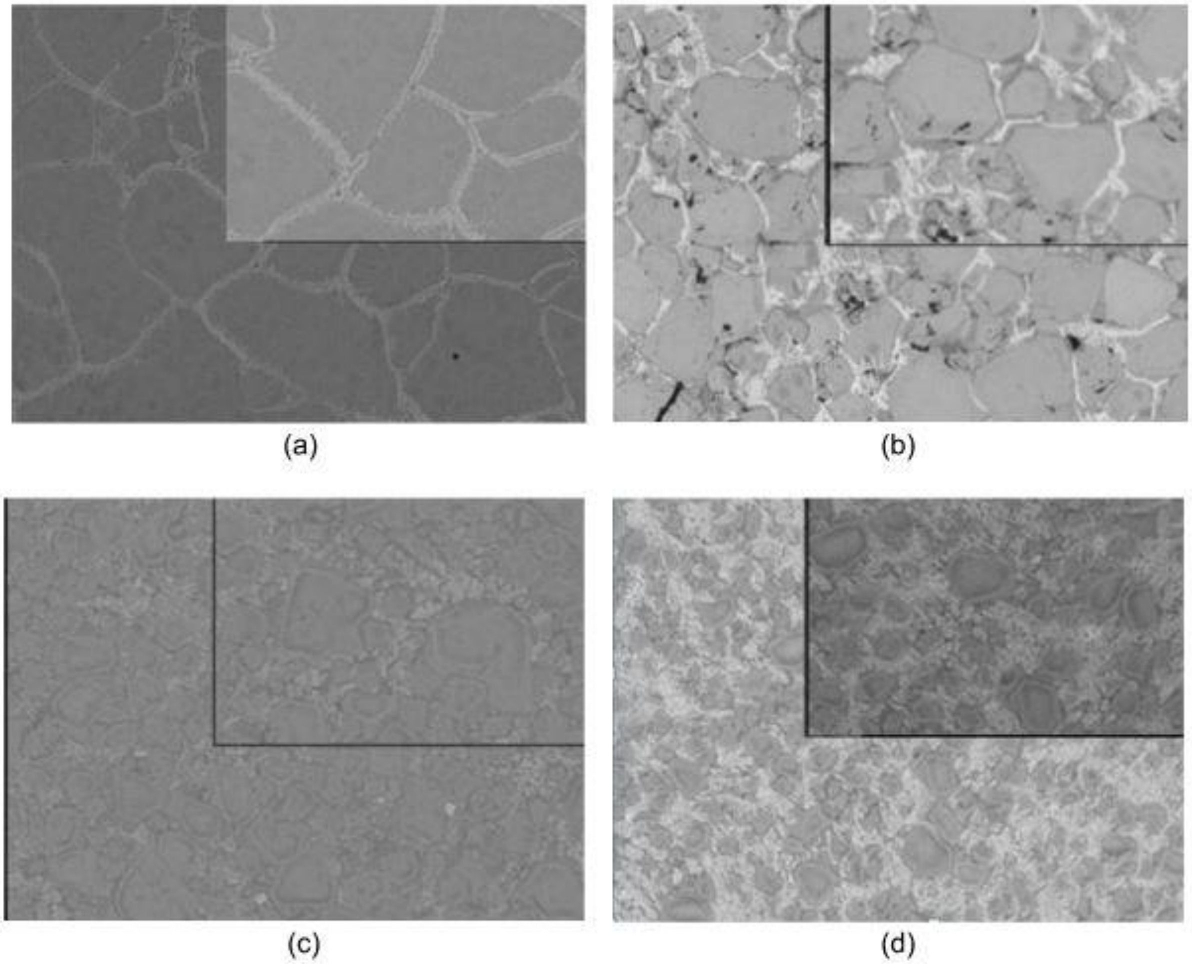

Fig. 2SEM micrographsof (a) Z0, (b) Z1, (c) Z3, (d) Z7

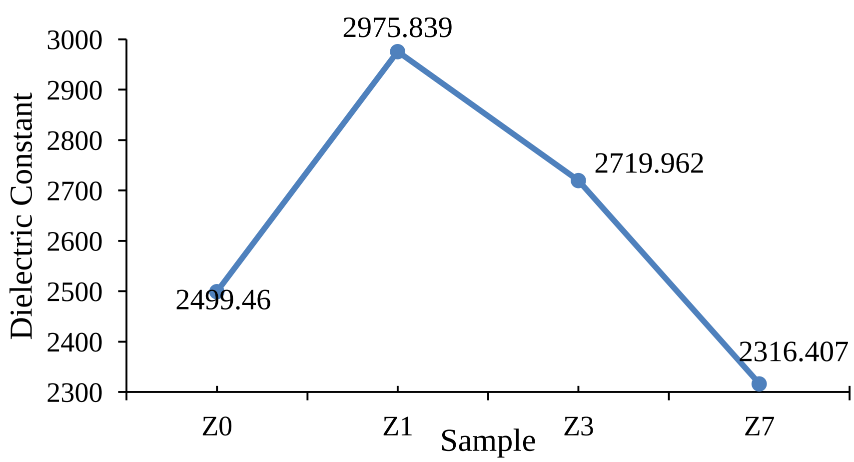

Fig. 3 Dielectric constant of ZBS doped CCTO samples Dielectric loss investigations were carried out at different composition of ZBS glass as shown in Fig.4. The dielectric loss of CCTO can be reduced with the

addition of ZBS glass dopant. The Z1 sample exhibited the lowest dielectric loss, measured at a high frequency 1 MHz, where sample show 1.02 loss value. This value is much lower than the undoped CCTO sample (1.35). As mentioned above, ZBS glass dopant can be used to improve the densification of CCTO ceramics. Therefore, this indicates that ZBS glass doping can be used to lowering the dielectric loss value of CCTO.

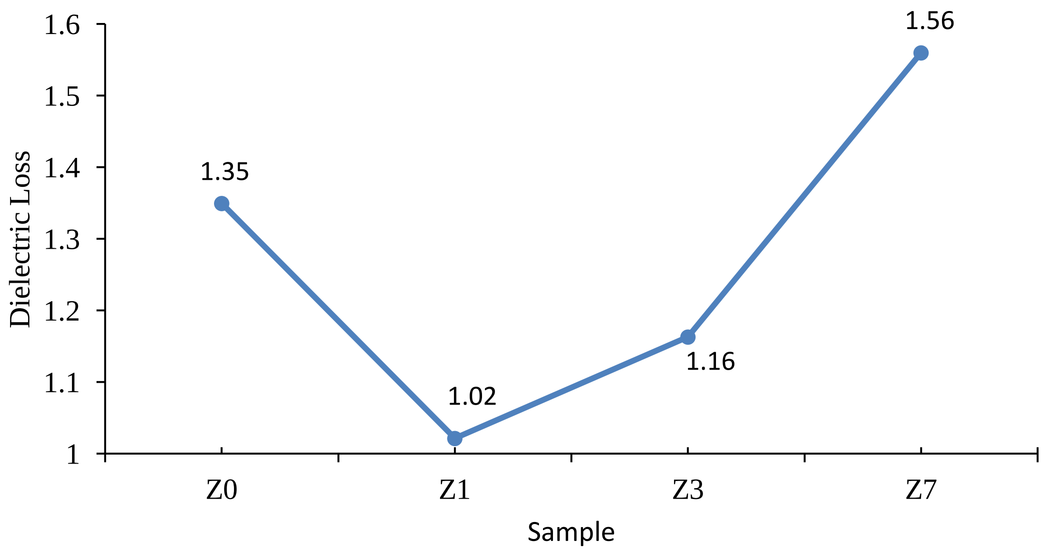

Fig. 4 Dielectric loss with different amount of ZBS glass

4. SUMMARY

The ZBS-doped CCTO ceramics samples were successfully prepared using solid state techniques. The densification and dielectric properties of CCTO ceramicsare strongly depends on the content of ZBS glass and chemical reaction between the glass and CCTO. For the samples added with large amount of glasses composition, a secondary phase was formed, which resulted in the deterioration of densification and dielectric properties. The highest relative density of 96%, the maximum dielectric constant of 3000 and lowest dielectric loss of 1.02 was obtained from the sample added with 1 mol % ZBS glass.

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