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# Effect of Borosilicate Glass Addition on the Dielectric Properties of CCTO-Glass Composites for DRA Applications

Mohd Fariz AB RAHMAN[1,a], Julie Juliewatty MOHAMED[2,b], Mohd Fadzil AIN[3,c] and Zainal Arifin AHMAD[1,d*]

[1]Structural Materials Niche Area, School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia.
[2]Advanced Materials Research Cluster, Faculty of Bioengineering and Technology, Jeli Campus, Universiti Malaysia Kelantan, Locked Bag No 100, 17600 Jeli, Kelantan, Malaysia.
[3]School of Electrical and Electronic Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia.

[a]mohdfarizabrahman@yahoo.com, [b]juliewatty.m@umk.edu.my, [c]eemfadzil@usm.my, [d]*srzainal@usm.my

**ABSTRACT.** The effect of borosilicate glass addition on the dielectric properties of CCTO-glass composites for DRA applications was studied. CCTO ceramics were prepared via solid state reaction method. The raw materials of CCTO were wet mixed for 24 hours and then dried overnight in oven. CCTO mixtures were calcined at 900 °C for 12 hours. The borosilicate glass, taken from laboratory beaker was grinded by using planetary ball mill machine to form a finer powder. Then the glass powder was mixed with CCTO's calcined powder for 24 hours. The mixed powder was compacted at 250 MPa and then was sintered at 1040 °C for 10 hours. X-Ray Diffractometer (XRD) analysis showed the formation of CCTO phase and minor secondary phase of CuO were obtained by pure CCTO and CCTO-borosilicate glass composites samples. Observation on Scanning Electron Microscopy (SEM) micrographs showed large grain size of CCTO was reduced with increasing borosilicate glass addition (0.01-1.0 wt.%). The $\varepsilon_r$ of CCTO was increased while the tan δ of CCTO was decreased with small addition of borosilicate glass. The resonance frequency of CCTO was moves to lower frequency with increasing of glass addition until 0.1 wt.%, but it moves to higher frequency with increasing of glass addition up until 1.0 wt.%. The radiation pattern shows that each sample can radiate the signal equally on E- and H-planes.

***Keywords:*** *$CaCu_3Ti_4O_{12}$, Borosilicate glass, Dielectric properties;*

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## 1. INTRODUCTION

Recently, wireless communication systems are growing rapidly where antenna is considered as one of the key devices for wireless communication systems. The trend of wireless communication devices is moving towards miniaturization in order to accommodate smaller designs and limited space. As being reported by Subramanian et al. [1], high dielectric constant, $\varepsilon_r$ (~ $10^4$) had been found on the oxide of $CaCu_3Ti_4O_{12}$ (CCTO) at low frequencies (1 KHz) and nearly constant over large temperature range from room temperature to 300 °C. Such material is very promising for the application as capacitor and dielectric resonator antenna (DRA). The important properties required for the ceramic material to be used as DRA are high $\varepsilon_r$, low dielectric loss (tan δ) and low temperature coefficient. However, even though CCTO is known to have high $\varepsilon_r$, it is also

identified to have high tan δ (>0.05). Yuan et al. [2] and Didry et al. [3] reported that tan δ of CCTO from their researches was around 1.0 at 1 MHz. Usually, high $\varepsilon_r$ will result in higher tan δ because of

inherent material properties. This phenomenon (high tan δ) happened not only for CCTO, but for other dielectric materials as well. Tan δ can be affected by several extrinsic factors, such as porosity, microstructural defects, impurities and microcracks [4].

Based on the previous studies, there were alternative ways to produce DRA with better properties; which is by using DRA composites. Even though there were various reports on ceramic composites used as DRA [5,6], there were no specific study on effect of borosilicate glass addition on the dielectric properties of CCTO and suitability for DRA application. Glass is known to have low tan δ and can improve the densification of ceramic materials. Previous study by Prakash and Varma [7] find that boron oxide and silicon oxide based glass can effectively reduce tan δ of CCTO from 0.12 to 0.06. Since the performance of antenna is evaluated by the dielectric properties ($\varepsilon_r$, and tan δ) of the material, thus borosilicate glass addition might help to modify the dielectric properties of CCTO.

## 2. MATERIALS AND METHODS

CCTO ceramics was prepared via solid state reaction method. The raw materials of $CaCO_3$ (Sigma Aldrich, >99%), CuO (Sigma Aldrich, >99%) and $TiO_2$ (MERCK, >99%) powder was wet mixed for 24 hours and the mixture was dried overnight in oven. The dried mixtures then were calcined at 900 °C for 12 hours. The borosilicate glass (Pyrex™), taken from laboratory beaker was grinded by using planetary ball mill machine to form a finer powder. Subsequently, the glass powder was mixed with CCTO's calcined powder for 24 hours in the ratio corresponding to the following chemical composition: (100-x) % $CaCu_3Ti_4O_{12}$ + x % glass additives (wt.%), where x = 0, 0.01, 0.1, and 1.0 respectively. The mixed powder was pressed into pellets under a pressure of 250 MPa. The sample was labelled as CCTO for pure CCTO sample while Boro0.01, Boro0.1 and Boro1 were stand for the samples of CCTO with addition of 0.01, 0.1 and 1 wt.% of borosilicate glass, respectively. The pellets then were sintered at temperature 1040 °C for 10 hours. The phase formation of the pure CCTO and CCTO-borosilicate glass composites were analyzed by using X-ray Diffraction (XRD) (model: Bruker Advance D8) while Scanning Electron Microscopy (SEM) (model: TM 3000) was used to observe the microstructures of the samples. For electrical measurement analysis, the dielectric properties of the samples were measured by using impedance analyzer machine (model: 4291B Hewlett Packard) at 1 GHz and for DRA behavior, the measurement was took placed by using network analyzer (model: HP8720D), spectrum analyzer (model: Agilent E4405B) and Swept Signal Generator (model: Agilent 83260B) machines.

## 3. RESULTS AND DISCUSSIONS

Fig. 1 shows the XRD pattern of pure CCTO and CCTO-borosilicate glass composites after being sintered at at 1040 °C for 10 hours. The amounts of glass added were 0.01, 0.1 and 1.0 wt.%. XRD analysis in Fig 1 showed that CCTO and CCTO-borosilicate glass composites samples present the formation of CCTO phase (ICDD Data File Card No. 01-075-2188) with minor peaks of CuO phases (ICDD Data File Card No. 00-045-0937). The minor CuO phase presented for each sample is expected come from the CuO compound that segregated at the grain boundary of CCTO. Previous studies [8-12] also reported that the presence of CuO compound was observed at the grain boundary of CCTO after being sintered at 1040 °C for 10 hours. According to Yuan et al. [1], the intergranular CuO phase is due to the instability (or activity) of Cu ions in the CCTO lattice. Cu ions were first separated out from CCTO at ~1000 °C, then were ousted to the surface layer of the pellet and mostly segregated at the grain boundaries, and were finally oxidized to CuO compound.

Fig. 2 shows the SEM images of the sintered pure CCTO and CCTO-borosilicate glass composites samples, respectively. It can be observed that the grain size of CCTO becomes smaller

with the increasing amount of borosilicate glass addition. Further addition of borosilicate glass contributed to the smaller grain size of CCTO. CCTO sample had the largest average grain size of 96.6 μm while Boro0.1 had

smallest average grain size with 54.05 µm. The glass addition seems to be segregated with CuO at the grain boundaries and restrict the CCTO's grain growth. Several researchers [13-15] stated that with more addition of glass into the $BaSrTiO_3$ (BST) and CCTO ceramics, the segregation of glass at the grain boundaries hinders the movement of ceramic particles, hence restricting the ceramic grain growth and reduce the grain size of BST and CCTO ceramics, respectively.

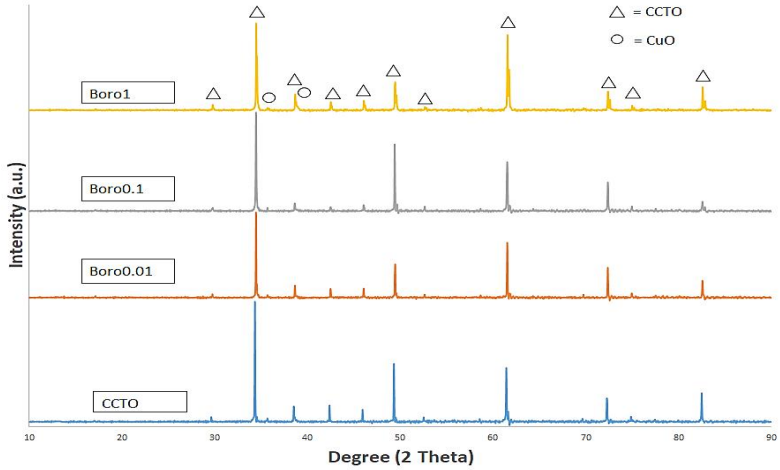


**Fig. 1** XRD pattern of sintered CCTO and CCTO-borosilicate glass composites samples

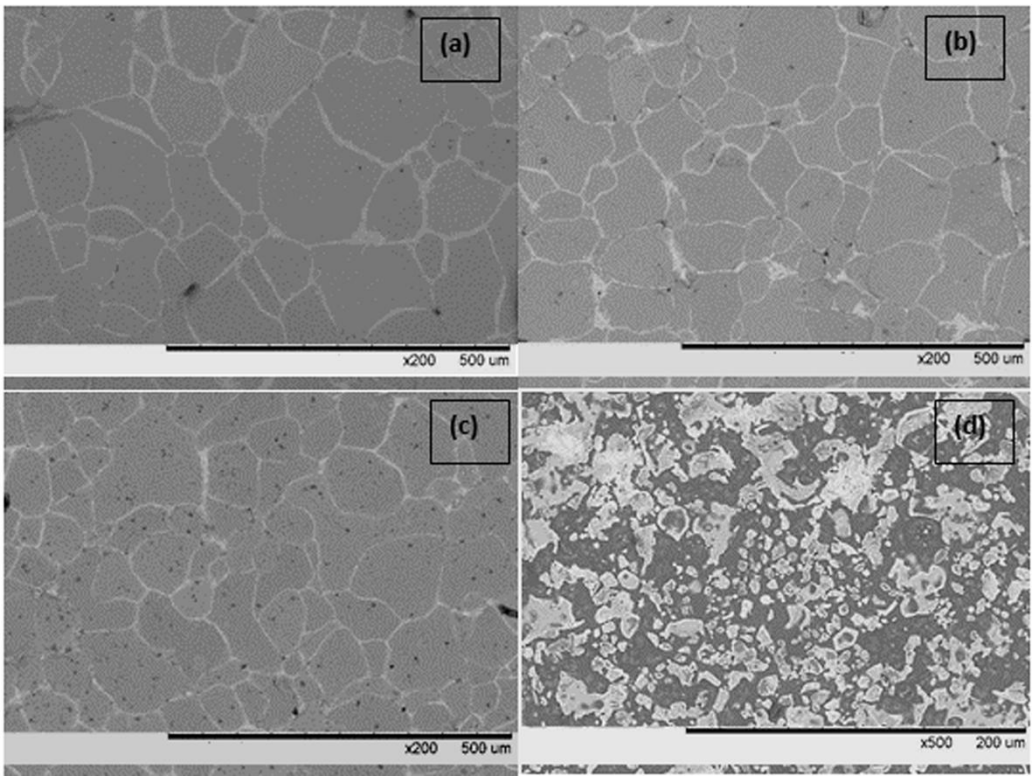


**Fig. 2** SEM micrographs of CCTO and CCTO-borosilicate glass composites samples with different glass composition of (a) 0 wt.%, (b) 0.01 wt.%, (c) 0.1 wt.% and (d) 1.0 wt.%

Table 1 shows the $\varepsilon_r$, tan δ and resonance frequency of CCTO and CCTO-borosilicate glass composites samples. It shows that as the composition of borosilicate glass in CCTO increased, the $\varepsilon_r$ of CCTO was increased as well while the tan δ of CCTO was decreased when all samples were measured at 1 GHz. The $\varepsilon_r$ of CCTO was increased from 86 to 100 while the tan δ of CCTO was decreased from 0.62 to 0.38 after the addition of 1.0 wt.% of borosilicate glass. The $\varepsilon_r$ of CCTO had increased while the reduction of tan δ of CCTO-glass composites because due to the addition of borosilicate glass improved the densification and reduce the porosity of the CCTO. Besides, it also was due to the properties of borosilicate glass that has low tan δ were added into the CCTO ceramics [7].

This table also shows the resonance frequency of CCTO moves to lower frequency from 9.51 GHz to 9.02 GHz with increasing of glass addition until 0.1 wt.%. Instead, the resonance frequency of CCTO was increased until 10.56 GHz when 1.0 wt.% of borosilicate glass was added into CCTO. The resonance frequency shifting was within the range of 9 to 11 GHz. According to International Telecommunication Union (ITU), this operating frequency is under the X-bands category [16]. Fechine et al. [5] stated that the shifting of the resonance frequency is caused by differences of $\varepsilon_r$ value of YIG ceramics as a function of doped $Gd_3Fe_5O_{12}$ compound where high $\varepsilon_r$ move the resonance frequencies to lower frequencies. Based on the dielectric results shown in Table 1, small addition of borosilicate glass increased the $\varepsilon_r$ of CCTO, thus contributed to lower resonance frequency of CCTO-borosilicate glass composites samples compared to the pure CCTO sample. But, when the addition of each glass was up to 1.0 wt.%, the $\varepsilon_r$ decreased, thus the resonance frequency of CCTO moves to the higher frequencies of 10.56 GHz.

**Table 1** $\varepsilon_r$, tan δ and resonance frequency of CCTO and CCTO-borosilicate glass composites samples.

| Sample | $\varepsilon_r$ at 1 GHz | tan δ at 1 GHz | Resonance frequency (GHz) |
|---|---|---|---|
| CCTO | 86 | 0.62 | 9.51 |
| Boro0.01 | 37 | 0.43 | 9.19 |
| Boro0.1 | 96 | 0.40 | 9.02 |
| Boro1 | 100 | 0.38 | 10.56 |

The radiation pattern in different plane of view of pure CCTO ceramics and CCTO-borosilicate glass composites samples were illustrated in Fig. 3. The measured radiation patterns were taken at the respective resonance frequency of each sample as shown in Table 1. For E-plane cut (Fig. 3(a)), it was observed that each sample that have been set up as DRA radiated the signal equally especially at the front and at the back lobes. It shows that each sample had a strong signals on the front and the back. However, there were dip at 90° and 270°, indicated that the transmission/reception signal by the sample was weak.

Meanwhile, Fig. 3(b) shows the H-plane cut of radiation pattern for the same samples. It can be observed that the radiation patterns for all samples were nearly identical between each other where the signal was radiated on the top of the plane. Similar kind of results also have been reported by Wan Ali et al. [6]. Furthermore, it can be observed that the radiation pattern of CCTO was increased after the addition of various glasses for both E- and H-planes. So, it can be said that the addition of borosilicate glass can help to improve signal strength to the CCTO when it is used as the DRA.

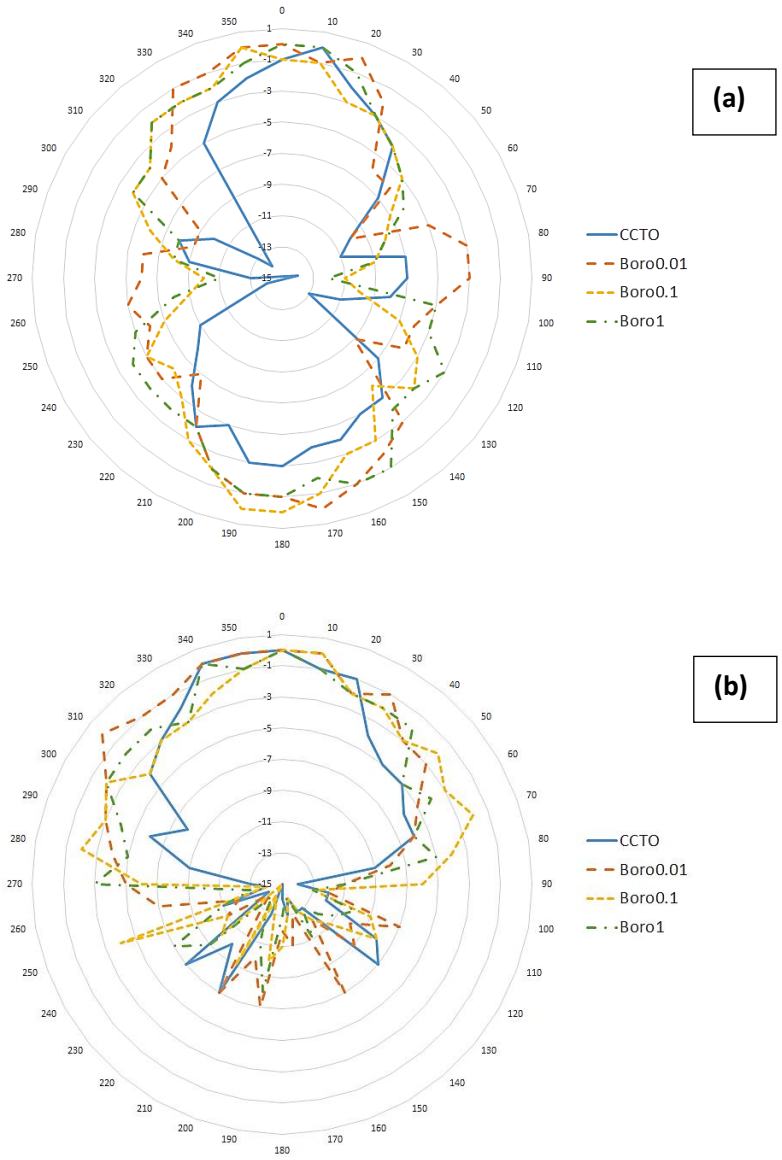


**Fig. 3** Radiation pattern of CCTO and CCTO-borosilicate glass composites samples as DRA in different cut plane (a) E-plane and (b) H-plane

## 4. SUMMARY

CCTO and CCTO-borosilicate glass composites were successfully prepared via solid state reaction method. From the XRD analysis, the formation CCTO phase alongside with minor CuO phase were seen for each sample which were sintered at 1040 °C for 10 hours. SEM micrographs show that the grain size of CCTO becomes finer with increasing glass concentration. The $\varepsilon_r$ of CCTO was increased while the tan δ of CCTO was decreased with small addition of borosilicate glass. The resonance frequency of CCTO was moves to lower frequency with increasing of glass addition until 0.1 wt.%, but it moves to higher frequency with increasing of glass addition up until 1.0 wt.%. The radiation pattern shows that each sample can radiate the signal equally on E- and H-planes. Thus, it shows that the borosilicate glass addition into CCTO can give the great effect on the dielectric properties of CCTO ceramics for DRA applications.

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