HEAT TREATMENT EFFECT WITH THE ELECTRODE CONTACT OF $CaCu_3Ti_4O_{12}$

Muhammad Azwadi Sulaiman[1], Sabar D. Hutagalung[1], and Zainal A. Ahmad[1]

[1]*School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia*

ABSTRACT

$CaCu_3Ti_4O_{12}$ (CCTO) has attracted a great attention for electronic devices miniaturization due to its very high dielectric constant properties at a wide range of frequency and nearly constant over broad temperature range. The origins of the giant dielectric constant have been speculated from electrical heterogeneous of interior elements of the CCTO ceramics. Four origins were suggested contributed to the electrical heterogeneous. In this study heat treatment were done with the electrode contact in Argon gas environment and the electrical properties over very wide frequency of CCTO ceramics were investigated. Cylindrical CCTO pellets samples were prepared by solid state reaction method and single phase of XRD pattern was obtained after sintering processes. Electrical impedance responds were measured at frequency from 100 Hz to 1 GHz for the samples for untreated and heat treated at 200ºC, 250ºC, 300ºC, 350ºC and 400ºC of CCTO. Improvement to the dielectric constant can be seen for 350ºC and 400ºC samples and dielectric loss were improved for 200ºC and 300ºC samples for overall frequency. The variations were discussed based on oxygen deficiency content and resistivity of the elements inside of CCTO structure.

ABSTRAK

$CaCu_3Ti_4O_{12}$ (CCTO) telah menarik perhatian tinggi untuk pengecilan peranti elektronik disebabkan sifat pemalar dielektrik yang sangat tinggi pada julat frekuensi yang luas dan hampir malar dalam julat suhu yang luas. Asal-usul pemalar dielektrik tinggi telah dispekulasikan daripada ketidakseragaman sifat elektrik unsur-unsur dalaman seramik CCTO. Empat asal-usul telah dicadangkan yang menyumbang kepada sigat heterogen elektrik tersebut. Dalam kajian ini, rawatan haba telah dilakukan bersama dengan elektrod dalam persekitaran gas Argon dan sifat elektrik terhadap frekuensi luas seramik CCTO telah kenalpasti. Sampel silinder CCTO telah disediakan oleh kaedah tindak balas keadaan pepejal dan fasa tunggal corak pembelauan XRD telah diperolehi selepas proses pensinteran. Respon elektrik impedan telah diukur pada frekuensi 100Hz hingga 1GHz untuk sampel tidak dirawat dan dirawat haba pada 200º C, 250º C, 300º C, 350º C dan 400º C daripada CCTO. Peningkatan kepada pemalar dielektrik boleh dilihat pada sampel 350º C dan 400º C dan kehilangan dielektrik telah bertambah baik untuk sampel 200º C dan 300ºC bagi keseluruhan frekuensi. Variasi tersebut telah dibincangkan berdasarkan kandungan kekurangan oksigen dan kerintangan elemen-elemen di dalam struktur CCTO.

Keywords: impedance, surface effect, dielectric, loss, high-k

INTRODUCTION

The developments in mobile and portable devices cause a high demand on miniaturization of electronic components [1–3]. The size of them is keep scaling down till hundreds nano-size in order to increase compactness of component simultaneously with increased functionality. This process take account of many parameters to ensure the properties of current materials can be maintain in such size or the other material should be looked as replacement.

Capacitors are important elements in electrical and electronic circuits, performing various functions that include blocking, coupling and decoupling, AC-DC separation, filtering, power factor correction, and energy storage. Capacitor component is size dependence for its capacitive properties. The properties are reduced by the reduction of plate area. So, in this case, higher dielectric material is required to maintain or increase the capacitance when the miniaturizing process is applied to the devices. If size are maintained, higher dielectric material will increase the capacitance and increase energy storage [4–6].

CCTO has attracted much interest because of its extraordinarily high permittivity (ε_r) of 10,000 at room temperature and very small temperature dependence in a broad temperature range from 100K to near 400K [7,8]. Furthermore, the dielectric constant of CCTO is almost frequency independent below 10^6 Hz, which is desirable for many micro-electronics applications [9]. Because of giant dielectric constant, CCTO can be used as dielectric material between two plates of capacitor to double its performance.

Researchers have come with several suggestions on the origin of high dielectric constant of CCTO. Surface oxidation layer effect [10–14], twin boundary layer [15–18], internal boundary layer capacitance [9,19] and planar defect within CCTO crystal [20–22]. However the constitutes of high dielectric phenomena is still remains controversial. Scanning probe and transmission electron microscopy have suggested that grains boundary insulative layer is being the dominant but the domain boundaries as the dominant were suggested too [16]. The complete pictures of the origins are unclear and were intensively discussed

In this study, effects of heat treatment with electrode in Argon environment were investigated at wide frequency range of impedance measurement. The electrodes were applied both of pellets surface during the heat treatment in order to investigate the surface layer contact between CCTO-electrode and other effects of the treatment. Electronic structure across semi conductive grains or grains boundary, insulative surface oxidation layer and conductive electrode were suggested formed barrier layer capacitance and reacted as an origin of high dielectric constant of CCTO.

METHODOLOGY

The same method as reported previously for $CaCu_3Ti_4O_{12}$ preparation was adopted [23]. First, the raw materials for $CaCO_3$, CuO and TiO_2 were prepared and weight according to the stoichiometric ratio for pure CCTO. The raw materials were mixed via ball milling process for an hour using an alumina jar Zirconia balls were used as the grinding media with mass ratio of balls to raw materials of 10:1. The well mixed raw material was calcined at 1000 °C for 3 hours and sintered at 1040°C for 4 Hours. Both calcined powder and sintered pellets were identified the phase formation by using X-ray diffractometer (XRD) (Bruker Advance D8). Sintered pellets were applied silver paste electrode both of surfaces and heat treated at 200°C, 250°C, 300°C, 350°C and 400°C in Argon gas environment for an 1 hour of soaking time with 5°C/m heating and cooling rate. All of the samples were measured electrical impedance for low frequency (100Hz to 1MHz) by using impedance gain spectroscopy and high frequency (1MHz to 1GHz) by using impedance analyzer (RF Impedance/Material Analyser 4291B Hewlett Packard).

RESULTS AND DISCUSSIONS

Typical x-rays diffraction pattern of as-sintered CCTO was obtained as shown on Fig. 1. The pattern were confirm the cubical perovskite single phase of CCTO and match to the standard ICDD number (01-075-2188). Recent researchers suggested that four elements contributed to the polarization of CCTO 1) electrode contact, 2)grain boundary layer, 3) domain boundary and 4) domain interior [24,25]. Heat treatments with the electrode were done in Argon environment in order to observed effect of the elements which origins of the high dielectric constant of CCTO. Argon gas environment were selected to prevent oxidation process to the silver electrodes and prevent further reoxidation of CCTO bulk ceramics.

The heat treatment should help to eliminate the residue air gap between the electrodes to the CCTO bulk and improve dielectric constant. Fig. 2 shows dielectric constant of untreated and heat treated CCTO pellets samples at low frequency measurement (100Hz to 1MHz). All of the samples exhibited the dielectric constant nearly constant from 100Hz to 100kHz and drop rapidly to out of MHz range. The trend were same for all sample but treated samples at 350°C and 400°C are higher than untreated, treated at 200°C, 250°C and 300°C.

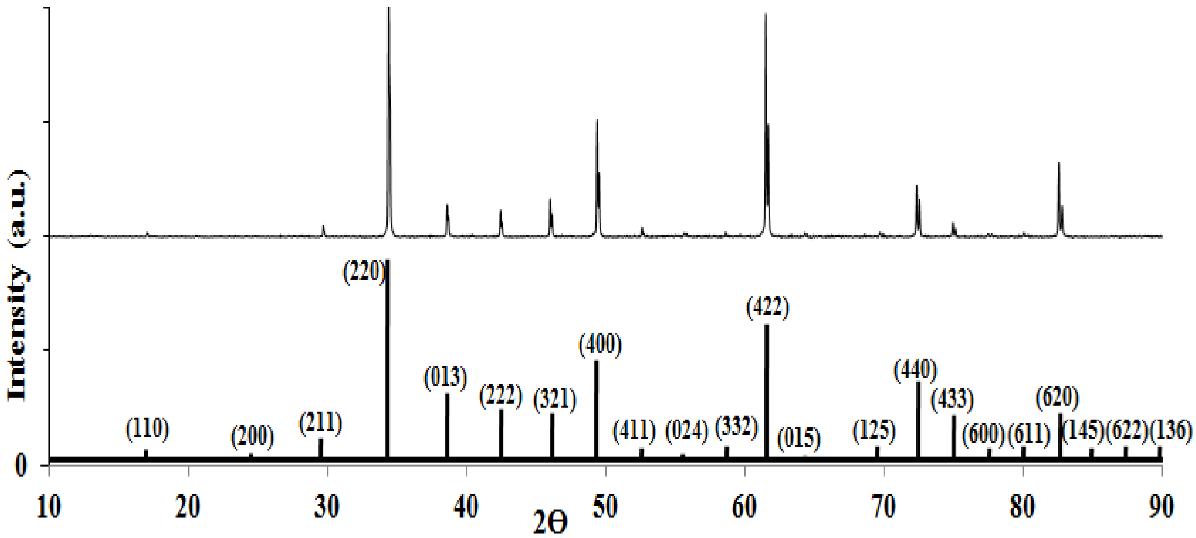

Figure 1: Typical X-ray diffraction patterns obtained from the as-sintered CCTO pellets and the standard

This variation are suggested based on oxygen absorption and chemisorb at grain and grain boundary from surface of CCTO pellets. Previous literature [26] reported grain boundary of CCTO contain very high oxygen content in form of CuO compared to the grain. Higher oxygen content of grains boundary will increase the resistivity [27,28]. Although Argon gas were supplied to the furnace chamber during the heating process, some residue oxygen gas still trapped inside the interior of CCTO sample because of slightly high degree of porosity. This can be seen from SEM micrograph at Fig. 3. All of the samples are capable to absorb the residue oxygen gas and increase the resistivity but sample of heat treated at higher temperature (350°C and 400°C) undergo chemisorb process of oxygen or the loss of oxygen at grain boundary and this will reduce the resistivity.

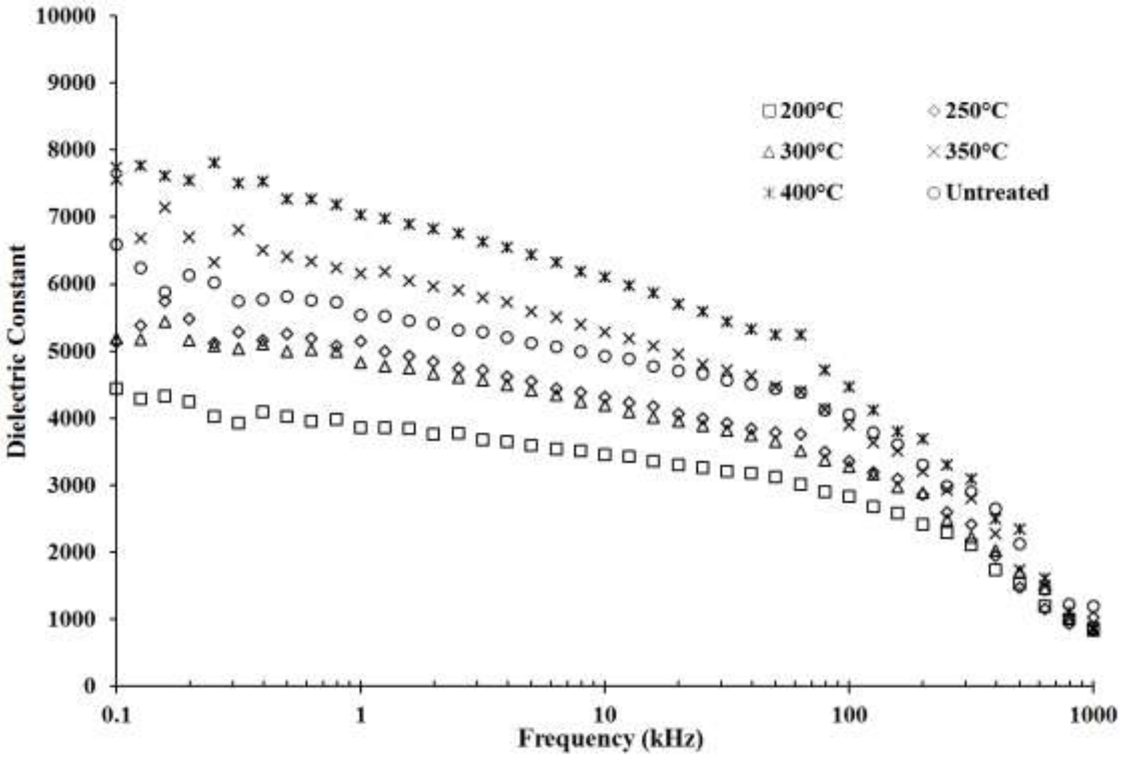

Figure 2: Dielectric constant of unheat treated (25°C) and heat treated CCTO (200°C, 250°C, 300°C, 350°C and 400°C) measured at low frequency (100Hz to 1MHz).

The losses of oxygen or the formation of oxygen vacancies during sintering process were widely reported [27,28] and the same phenomena happen to high temperature treatment samples [29]. The low partial pressures of oxygen at heating environment also allow desorption process of the oxygen at grain boundary and leave oxygen vacancies site. This can be seen on Fig. 4, samples of heat treated at 200°C, 250°C and 300°C undergo adsorption of oxygen gas and lowered resistivity of grains boundary and affected to low dielectric constant properties (>1MHz).

SEM Micrograph as shown from Fig. 3 consisted of high porosity with grains of incomplete neacking process. This is happen because of high calcination temperature to the after mixed CCTO raw constituent material and insufficient pressure during the forming process to form dense pellets. Higher porosity caused lower dielectric constant and lower dielectric loss for overal frequency range. High porosity of CCTO pellets were suitable to be used as gas and humidity sensor.

Fig. 4 show dielectric loss of untreated and heat treated CCTO sample at low frequency. Most of the sample shared a constant trend about 0.2 and below of dielectric loss from 100Hz to 100kHz and the value raised gradually exceeding MHz range of frequency as the process of relaxation phenomenon to the grain interior or domain boundary were responded. Low and medium frequency were suggested by literatures contributed from grains boundary and electrode contacts. Adam et al [30] reported the effective dielectric for ceramics therefore associated with the presence of either thin, reoxidized of grain boundary region on the outer surface of large semiconducting grain.

Later there were found that grains were consisted of many tiny domains which associated to domain and domain boundary[17,25,31,32]. The relaxation peak at high frequency as shown on Fig. 4 was associated to domain boundary resistivity. Grain boundary contributed to relaxation should be fall at low frequency. Lower frequency measurement should see the effects of grain boundary and electrode as the trend shown on the Fig. 4 the dielectric loss before 100Hz of frequency. The dielectric loss should be higher as another relaxation phenomenon associated with grain boundary effects.

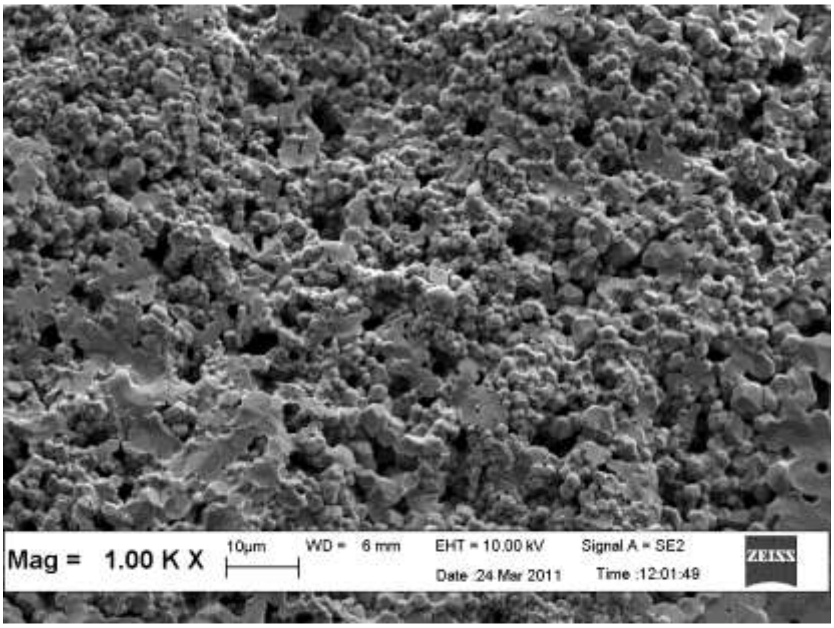

Figure 3: SEM Micrograph of as-sintered CCTO microstrcuture.

Our previous study on Nb-Doped CCTO [32] was found three relaxation peak of the three elements (electrode, grains boundary and domains boundary) of CCTO electrical responds which visible only two elements in this heat treated study. This is because of fine grains size effect and absence of any donor dopant element to increase N-Type of interior of CCTO.

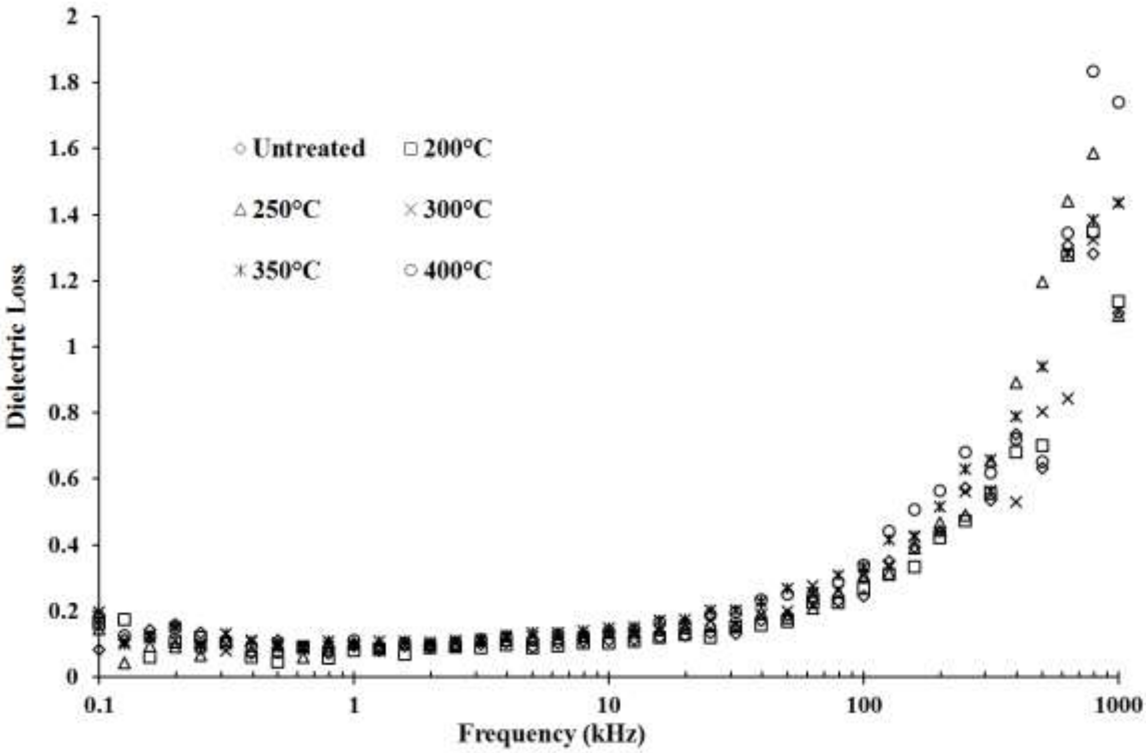

Figure 4: Dielectric loss of unheat (25°C) and heat treated CCTO (200°C, 250°C, 300°C, 350°C and 400°C) measured at low frequency (100Hz to 1MHz).

Sinclair et. al [19] reported the exterinsic nature of CCTO electrical impedance and can be described as two sets of parallel of resistor (R) and capacitor (C) connected in series. Each set of RC element represents resistivity and capacitance of elements of the CCTO microstructure. Fig. 5 shows impedance complex plane of untreated and heat treated CCTO at low frequency. Because of out of measurement frequency range, there are insufficient of data to plot curve fitting to measure the resistivity of grain boundary that contributed to the electrical responds but the value can be estimated are over MΩ.com range [25]. As a comparison from Fig. 5, heat treated at 400ºC and 350ºC have lower grain boundary resistivity compared to the other samples and caused higher dielectric constant propeties at the low frequency range.

Single curve low frequency impedance complex plane indicated the absence of electrode contact effect at the measurement range. This may caused by very high resistivity on the grain boundary was overlapping the resistivity of electrode contact as the both respond at nearly same frequency range.

Fig. 6 shows dielectric constant of untreated and heat treated CCTO at high frequency (1MHz to 1GHz). Continuation of the reducing of dielectric constant from Fig. 2 can be seen on the Fig 3. Dielectric constant decreased to about 10MHz and nearly constant till 1GHz. There are not large variationss at high frequency between the samples except the untreated CCTO showed the lowest dielectric constant than the others. Literatures suggested high frequency responds of dielectric constant is contributed by domain and domain boundary inside of CCTO grains.

From the SEM micrograph, domains existence were fail to be discovered. This is because of fine and small grains very hard to found the domain as reported by Fang et al [33]. All heat treated samples were affected by the treatment and improve the dielecric constant properties. Semiconducting domain and insulative domain boundary as the third internal boundary layer capacitance and was discovered at high frequency measurement only [25,31,34]. There is no clear reason to the increasing of dielectric constant to the heat treated sample. This may come from restructuring of the domain boundary thickness and the size.

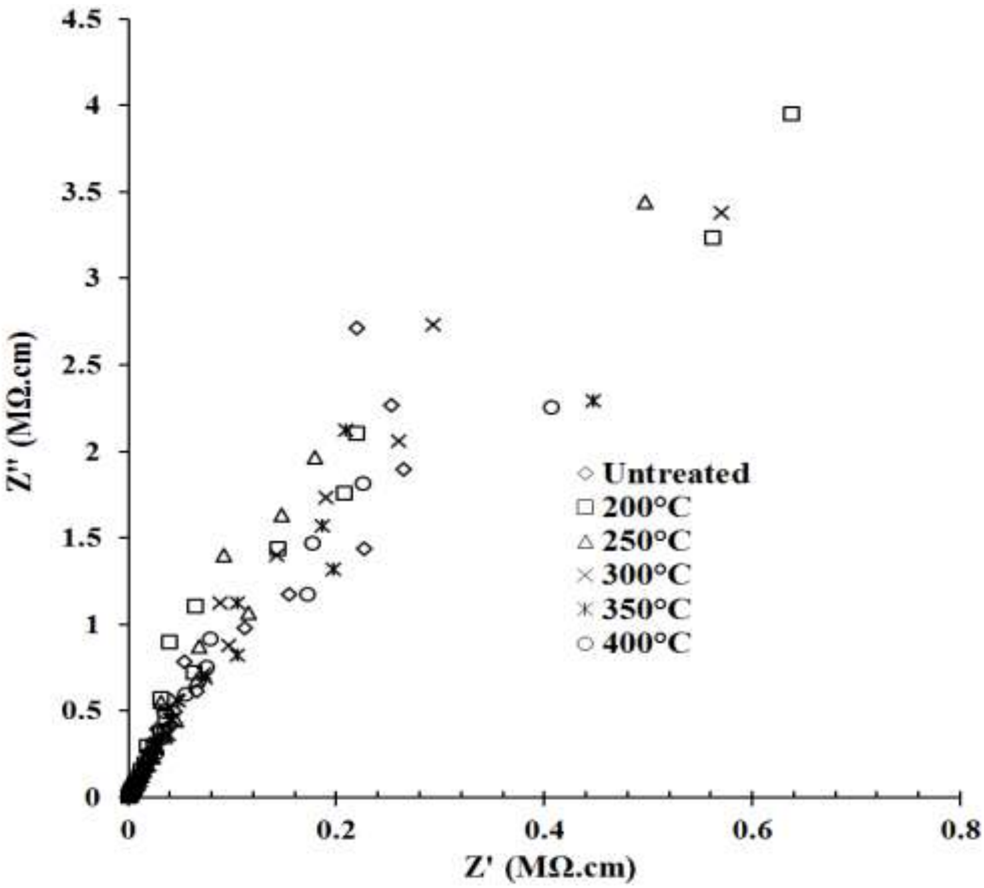

Figure 5: Impedance complex plane of unheat treated (25°C) and heat treated CCTO (200°C, 250°C, 300°C, 350°C and 400°C) measured at low frequency (100Hz to 1MHz).

Dielectric losses of untreated and heat treated CCTO samples at high frequency are shown on Fig. 7. Relaxation peak can be seen continuation from Fig. 4 is related to domain boundary resistance. Most of them show same trend except the untreated CCTO. Untreated and heat treated at 400°C of CCTO samples show very high dielectric loss (above 2.31 at 1MHz). At 200MHz of frequency, untreated sample dominated till 1GHz (0.16).

Sample of heat treated at 200°C and 300°C are among the lowest for overal frequency but at very high frequency, all heat treated samples have nearly same dielectric loss till 0.001 before become negative value. At very high frequency (>200MHz), the negative resistance phenomenon were occurred to the all heat treated CCTO samples. There is no clear reason for the negative value and the variation of dieletric loss between samples. This may caused by diodes behavior of the domain interior to react as varistor like responds at very high frequency (>800MHz). There are limited knowledge of literatures regarding the domains effect to the treatment of CCTO to compare.

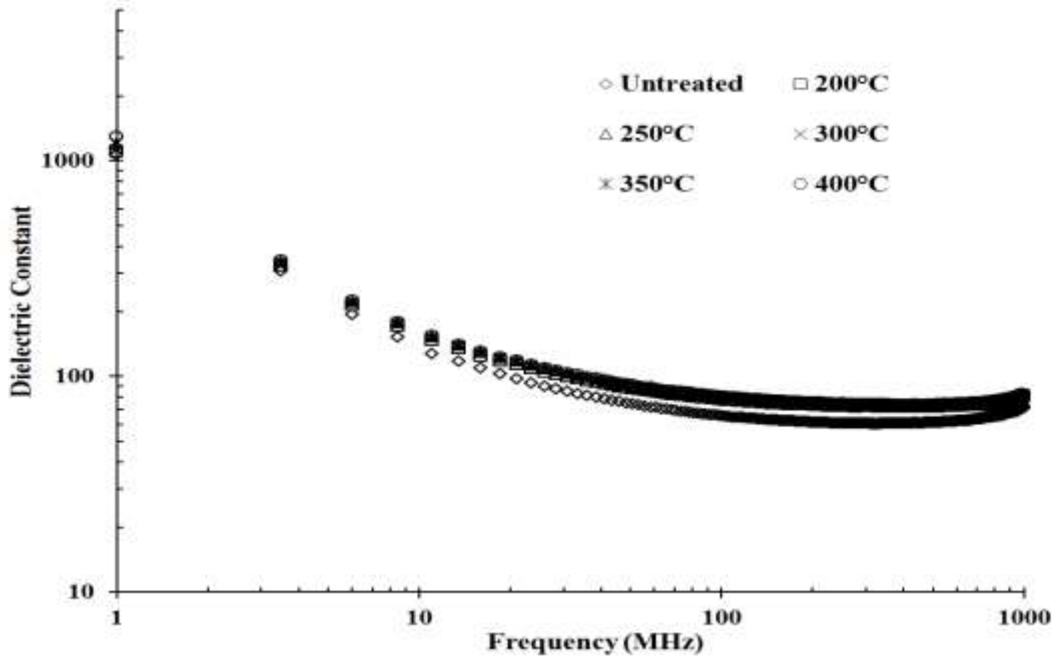

Figure 6: Dielectric constant of unheat treated (25°C) and heat treated CCTO (200°C, 250°C, 300°C, 350°C and 400°C) measured at high frequency (1MHz to 1GHz).

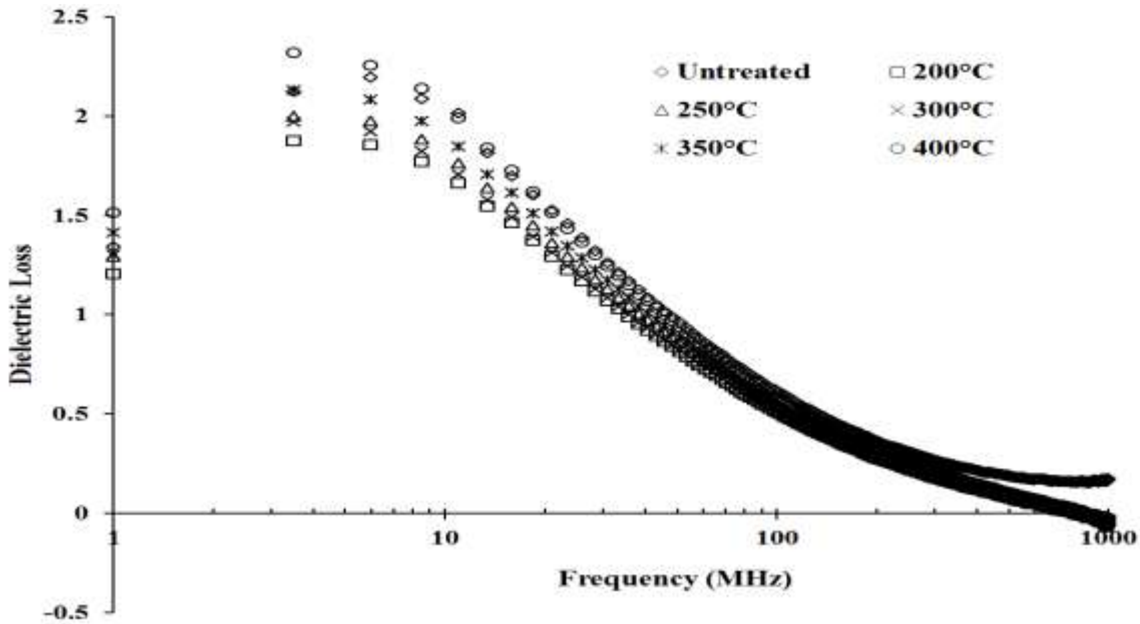

Figure 7: Dielectric loss of unheat treated (25°C) and heat treated CCTO (200°C, 250°C, 300°C, 350°C and 400°C) measured at high frequency (1MHz to 1GHz).

Fig. 8 shows impedance complex plane of untreated and heat treated CCTO at high frequency. Two curve were clearly shown and the high resistivity curve is continuation from the low impedance curve. Resistivity of the responded elements of the curve can be identified by using curve fitting of the semicicle to the Z' axis. From the curve fitting, heat treated at 400°C of CCTO had a lowest resistivity followed by heat treated at 350°C, 250°C, untreated samples, 300°C and 200°C as the highest.

The impedance was clearly shown the interior of domains exhibited very low resistivity or semiconducting state. Semiconducting domain and insulating domain boundary created boundary layer capacitance and major origins of high dielectric constant at high frequency region. Heat tretment effect to the domain boundary resistivity are suggested same to the effect to grain boundary because of the impedance patterns showed the same pattern with high temperature treated CCTO (350ºC and 400ºC) have low resistivity.

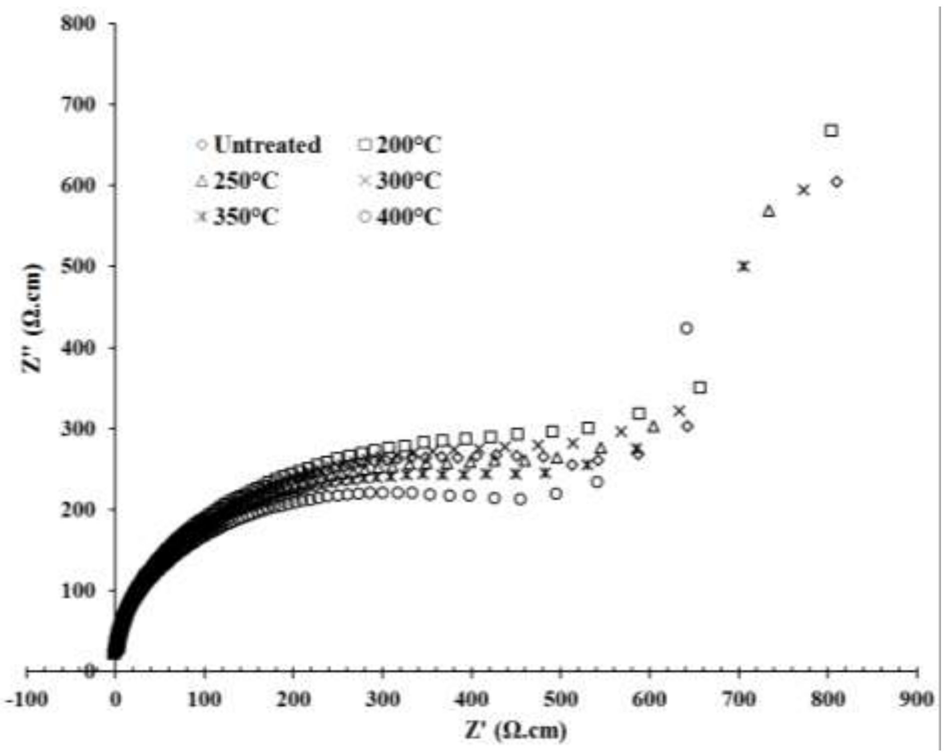

Figure 8: Impedance complex plane of unheat treated (25°C) and heat treated CCTO (200°C, 250°C, 300°C, 350°C and 400°C) measured at high frequency (1MHz to 1GHz).

CONCLUSIONS

Heat treatment effects to the origins of electrical responds of CCTO were investigated. Heat treatment in Ag environment at high temperature can increase dielectric constant of CCTO for overall frequency. This can be described by the increasing of oxygen deficiency as temperature of heat treatment increased. Heat treatment at 300 shows the best option because of increase of dielectric constant and lowering the dielectric loss.

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