Low temperature sintered giant dielectric permittivity $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ sol-gel synthesized nanoparticle capacitors

Venkata Sreenivas Puli^{*,†}, Shiva Adireddy^{*}, Manish Kothakonda^{*}, Ravinder Elupula[†]
and Douglas B. Chrisey^{*}

^{*}Department of Physics and Engineering Physics, Tulane University
New Orleans, LA 70115, USA

[†]Department of Chemistry, Tulane University, New Orleans, LA 70115, USA

[†]pvsri123@gmail.com

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This paper reports on synthesis of polycrystalline complex perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (as CCTO) ceramic powders prepared by a sol-gel auto combustion method at different sintering temperatures and sintering times, respectively. The effect of sintering time on the structure, morphology, dielectric and electrical properties of CCTO ceramics is investigated. Tuning the electrical properties via different sintering times is demonstrated for ceramic samples. X-ray diffraction (XRD) studies confirm perovskite-like structure at room temperature. Abnormal grain growth is observed for ceramic samples. Giant dielectric permittivity was realized for CCTO ceramics. High dielectric permittivity was attributed to the internal barrier layer capacitance (IBLC) model associated with the Maxwell–Wagner (MW) polarization mechanism.

Keywords: CCTO; cubic; giant dielectric permittivity; IBLC; grain growth.

1. Introduction

High dielectric permittivity materials with weak temperature dependence have been playing a significant role in microelectronics industry. They have been used as important devices such as capacitors, memory devices, resonators, filters and have potential use in various modern microelectronics and electromechanical applications. Ternary oxide, calcium copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ -CCTO) is a ($\text{A}'\text{A}''\text{B}_4\text{O}_{12}$) type perovskite structured material with 1:3 order at A-site, where the oxygen octahedra are strongly tilted and Cu cations occupy the A'' site, Cu atoms on the A site cause tilting of the TiO_6 octahedral, which adapts a four-fold square-planar coordination at doubled simple perovskite lattice cell indexed as cubic structure with $\text{Im}\bar{3}$ space group.¹ The high dielectric permittivity [$\epsilon \sim 12,000$ – $300,000$ over a wide range of temperature 0°C – 450°C] phenomenon was firstly observed in CCTO ceramics.^{1–15} There has been great interest in the properties of CCTO since the discovery of the unusual high dielectric permittivity.⁴ CCTO received considerable attention due to colossal dielectric permittivity.⁵ Usually, ferroelectric materials show high dielectric permittivity near its Curie temperature, which is typically associated with a phase change in the crystal structure, whereas CCTO-based materials show weak temperature-dependent dielectric properties over a wide range of temperature (-173°C to 330°C).⁵ Later, high dielectric permittivity in ($\epsilon \sim 300,000$) polycrystalline CCTO ceramics was reported by West *et al.*⁶ They also demonstrated that according to impedance

spectroscopy CCTO ceramics are electrically heterogeneous and consist of semiconducting grains with insulating grain boundaries. The extrinsic giant-dielectric permittivity of CCTO ceramics is therefore attributed to a grain boundary (internal) barrier layer capacitors (IBLC).^{6–8} In this case, polarization is created between the semiconducting grains and insulating grain boundary region of ceramic samples.

However, dielectric properties of CCTO capacitors are very sensitive to different synthesis methods and processing parameters. The scientific reason behind this variation in dielectric properties is not yet completely understood and different mechanisms were attributed to giant dielectric properties in these CCTO-based materials.⁹ West *et al.* also reported that the origin of the high permittivity in nonferroelectric CCTO-based materials could be attributed to space charge polarization and is not an intrinsic property associated with the crystal structure and in particular these materials were used in IBLCs due to the development of Schottky barriers at grain boundaries.^{6–8} As stated earlier, in contrast to relaxor-type of materials, another important feature of CCTO is relatively weak temperature dependence of the dielectric response (between ~ 100 and 600 K).⁵ The temperature independence or weak temperature dependence of this exceptionally large dielectric permittivity CCTO is unique. Colossal permittivity in CCTO single crystals, epitaxial thin films can be associated with an extrinsic electrode-sample interface effect.^{5,9,10}

Recently, lead-free body centered cubic perovskite like $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO), and nonperovskite $\text{Li}_x\text{Ti}_{0.1}\text{Ni}_{1-x}\text{O}$

(LTNO)-based materials with giant dielectric permittivity ($\epsilon \sim 10^4$ – 10^5 @ kHz region frequency) values received notable attention for various applications.^{1–15} High dielectric permittivity in this type of materials is an extrinsic property associated with Maxwell–Wagner (MW) polarization (interfacial polarization), which often arises in a material consisting of semiconducting grains, while grain boundaries are insulating.^{13–15}

In this paper, we report the investigations of structural, dielectric and impedance spectroscopic properties of CCTO nanoparticles using X-ray diffraction (XRD), Raman spectroscopy, dielectric and impedance spectroscopy techniques. CCTO ceramic powders were prepared by sol–gel auto combustion synthesis route at low sintering temperature. Sol–gel auto combustion synthesis route is one of the easiest and efficient routes for producing ceramic materials with excellent process control with improved properties. XRD is used for possible signature of structural information. Detailed analysis of dielectric and impedance data was carried out to infer the giant dielectric permittivity behavior of CCTO ceramics.

2. Experimental Procedure

CCTO ceramics was synthesized by the sol–gel method. Calcium acetate hydrate ($\text{CaC}_4\text{H}_6\text{O}_4$ 99%), copper (II) acetate anhydrous ($\text{Cu}(\text{CH}_3\text{COO})_2$, 98%), titanium (IV) isopropoxide ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, 97%) (All chemicals were reagent grade from Alfa Aesar, USA) were weighed according to the stoichiometry. All precursors were dissolved in the acetic acid, ethanol and 2 methoxyethanol separately and were homogenized by magnetic stirring for 2 h at 80°C. Once all the precursors were completely dissolved individually, Ca^{2+} and Cu^{2+} precursor solutions were added to titanium precursor drop by drop in glove box and were homogenized by magnetic stirring for 2 h at 80°C. The homogeneously mixed solution was then placed on the hot plate to form a gel and the obtained gel was dried at 180°C on the hot plate for 24 h and dried to blue colored powders. The powders were calcined at

800°C for 3 h. Phase identified powders were made into pellets by uniaxially pressing in a die with an applied pressure of 2 MPa. The calcined powder was pressed into green pellets (13 mm in diameter) and sintered at two different sintering temperatures (T_s) 1050°C, 1100°C for sintering times (S_T) 8 h, 30 h in air, respectively, in a Carbolite box furnace (High Temp Box Furnace 1700C 10L 208/240, UK) with heating and cooling rates of 10°C/min. The prepared green pellets were characterized by XRD (D8 Discovery X-ray diffractometer with $\text{Cu K}\alpha$ radiation, $\lambda = 1.54 \text{ \AA}$; Philips, The Netherlands). Particle size analysis of the CCTO as-prepared particles was investigated using transmission electron microscope (TEM FEI G2 F30 Tecnai TEM operated at 200 kV). The morphology (microstructure) of the sintered ceramic samples was investigated by scanning electron microscope (SEM Hitachi S-4100, Tokyo, Japan). EDX analyzer (model Inca Xmax, Oxford, UK) was used for elemental analysis.

For electrical characterization, pellet faces were slightly polished with SiC paper until it reached a thickness of 0.6 mm, and silver painted pellets were dried at 200°C for 2 h for better electrodes. The dielectric measurements (dielectric permittivity, dielectric loss, and impedance spectroscopy) were performed over the frequency range of 100 Hz to 1 MHz and temperature range of 30–160°C with an applied rms voltage of 1 V using a LCR meter analyzer (Agilent 4294A 40 Hz–110 MHz Precision Impedance Analyzer, USA). Each measured temperature was kept constant with an accuracy of $\pm 5^\circ\text{C}$.

3. Results and Discussion

3.1. Structural characterization of CCTO nanoparticles

Figure 1 shows the XRD patterns of ceramics, sintered at 1050°C for 8 h (CCTO1) and 1100°C for 30 h (CCTO2), respectively. For these ceramic pellets, the diffraction patterns could be indexed to a body-centered cubic perovskite-related structure of space group $Im\bar{3}$. The XRD patterns are matched with the CCTO standard JCPDS file. All the CCTO diffraction

Fig. 1. XRD patterns for CCTO1, CCTO2 ceramics pellets sintered at 1050°C (8 h) and 1100°C (30 h).

peaks were indexed based on the body-centered cubic unit cell (JCPDS 75-2188), confirming the formation of a major phase of CCTO along with some minor phases of TiO_2 , CuO .^{16–18} This indicates that the sintering conditions in this work have caused observable decomposition of CCTO ceramic pellets. However, the higher sintering temperature and time could not significantly change the presence of secondary phases, as shown in Fig. 1. The lattice parameters were calculated, being $a = 7.277 \text{ \AA}$, unit cell volume $V = a^3 \sim 385.3530$ for the 8-h-sintered sample and $a = 7.249 \text{ \AA}$ cell volume $V = a^3 \sim 381.0165$ for the 30-h-sintered samples, respectively. The obtained lattice parameters are almost matching with the literature values ($7.391 \text{ \AA}$ and $7.373 \text{ \AA}$).¹⁸ The crystallite size was evaluated using the XRD peaks according to the Scherrer equation: $D = 0.94\lambda/(\beta \cos \theta)$, where λ is the x-ray wavelength, and β is the half maximum diffraction peak width. The calculated values of D are 55–60 and 70 nm for CCTO1, CCTO2, respectively. The density of ceramics is calculated using XRD results: The densities of the pellets are 4.5 g/cm^3 for the 8 h sintered sample and 4.9 g/cm^3 for the 30 h sintered sample, respectively. It can be seen that the mass density of the CCTO ceramics increases with progressive increase in sintering temperature and sintering time. The increase of mass density with sintering temperature/and or time is attributed to the decrease of porosity. These results are consistent with that of SEM morphologies as discussed in the below section.

Raman Spectroscopy

Raman spectra of CCTO1, CCTO2 pellets sintered at different T_s and T_r are depicted in Fig. 2(a). All the prominent Raman modes $\text{Ag}(1) \sim 448 \text{ cm}^{-1}$, $\text{Ag}(2) \sim 517 \text{ cm}^{-1}$, $\text{Fg}(2) \sim 448 \text{ cm}^{-1}$, $\text{Fg}(3) \sim 581 \text{ cm}^{-1}$ corresponding to CCTO ceramics were detected respectively. The detected Raman modes are in agreement with earlier reports,^{17,19} however, there is a little shift in the mode positions with respect to the reported data. The presence of Raman modes — $\text{Ag}(1)$, $\text{Ag}(2)$ and $\text{Fg}(2)$ — was attributed due to TiO_6 rotation-like lattice vibrations, whereas the other mode $\text{Fg}(3)$ is associated

with a O–Ti–O anti-stretching vibration.^{17,19} As reported by Rainer Schmidt *et al.*, $\text{Ag}(1)$ mode forms a double peak structure with the $\text{Fg}(2)$ mode with a slight shift in Raman mode towards high frequency region.^{17,19} There is not much change in lattice vibrational modes as observed in the Raman spectroscopic data for both CCTO1, CCTO2 pellets sintered at different sintering temperatures (T_s) (1050°C @8 h, 1100°C @30 h). However, noticeable changes in electrical properties particularly for dielectric properties have been detected. It can be concluded from Raman Spectroscopy that the data are not sensitive to the sintering temperature and sintering time of these sol–gel synthesized CCTO ceramics.

Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM)

As synthesized CCTO nanoparticles, TEM images (Fig. 2) have shown an average particle size of $\sim 50\text{--}70 \text{ nm}$. It can be clearly seen from TEM images, that the CCTO nanoparticles have shown core-shell type morphology. It is believed from the literature that during the processing of CCTO, insulating surfaces form on semiconducting grains creating an electronically heterogeneous material, which is very similar to that reported for.^{6–9}

Figure 3 shows the microstructure's top surface and fractured surfaces (Figs. 3(b) and 3(c)) of the ceramics sintered at 1050°C for 8 h and 1100°C for 30 h, respectively, indicating an abnormal growth in the grain size with increasing sintering temperature and time. SEM images revealed bimodal distribution of the grains with clear grain boundaries. The small grains are distributed among the large grains of few micrometers. Whereas, SEM image of CCTO2 ceramics sample have shown abnormal grain growth when compared to CCTO1. The average grain sizes are about $10\text{--}40 \mu\text{m}$ for the 8- and 30-h sintered samples, respectively. This abnormal grain growth is also due to evolution of a small amount of excess intergranular phase of CuO which is eutectic with TiO_2 .^{20–24} CuO enhances the densification of dielectric materials via a liquid phase sintering mechanism, and is known to segregate at the grain boundaries in CCTO

Fig. 2. Raman Spectroscopic patterns for CCTO1, CCTO2 ceramics pellets sintered at 1050°C (8 h) and 1100°C (30 h) and Transmission electron microscopic (TEM) images of as synthesized CCTO nanoparticles.

Fig. 3. (a) Scanning electron microscopic images (top surface of pellets) and EDX images, (b), (c) fractured SEM surfaces for CCTO1, CCTO2 ceramics pellets sintered at 1050°C (8 h) and 1100°C (30 h).

ceramics.^{20–24} The EDX measurements confirmed the presence of Ca, Cu, Ti, and O in CCTO (CCTO1, CCTO2) ceramics. The atomic percentage of Ca, Cu, Ti, and O in CCTO ceramics at grain and grain boundaries obtained from EDX analysis is listed in Table 1.

3.2. Dielectric properties

Studies in dielectric and electrical properties provide insight into the localized electric charge carriers which leads to the understanding of electrical conduction mechanism and

dielectric polarization. Figure 4 shows the variation in the dielectric permittivity (ϵ) of CCTO1, CCTO2 ceramics as a function of temperature (30–160°C) at some fixed frequencies (100 Hz–1 MHz). The ϵ values for the CCTO1, CCTO2 ceramics at room temperature (30°C) at 100 Hz were ~ 9131 , ~ 52562 , respectively. A step like decrease of the dielectric permittivity at low frequency and high temperature to high frequency is observed from Fig. 4. Rapid increase in the dielectric permittivity at low frequency and higher temperature is attributed to the interfacial space charge polarization [MW polarization relaxation, where the charge carriers accumulate at the interface of semiconducting grains and insulating grain boundary] mechanism.^{11,12} As well, decrease of ϵ with increase of frequency can be described in terms of the interfacial space charge polarization. The dielectric permittivity increases slowly with increase in temperature. Subsequently, the dielectric permittivity rapidly reaches a maximum of 10^5 orders of magnitude with increase in temperature up to its maximum value. Notably, CCTO2 ceramic samples have shown enhanced values of dielectric permittivity with increasing sintering temperature and time (1100°C@ 30 h), when compared to CCTO1 ceramic sample

Table 1. EDX atomic wt.% analysis for CCTO1, CCTO2 ceramics pellets sintered at 1050°C (8 h) and 1100°C (30 h).

Element	Grain (8H) (Atomic %)	Grain boundary (8H) (Atomic %)	Grain (30H) (Atomic %)	Grain boundary (30H) (Atomic %)
O K	68.88	30.84	69.64	59.04
Ca K	3.97	7.22	4.24	6.34
Ti K	14.99	34.77	10.52	22.17
Cu K	12.16	27.18	15.60	12.45

Fig. 4. (a), (b) Variation of dielectric permittivity (ϵ) with frequency at different temperatures for CCTO1, CCTO2 ceramics pellets sintered at 1050°C (8 h) and 1100°C (30 h).

sintered 1050°C for 8 h. The dielectric permittivity of these ceramic samples changed drastically with the modification of the grain size.^{9,18,23,24} The high dielectric permittivity in CCTO [CCTO1, CCTO2] ceramics is attributed to the presence of large grains and the presence of grain-boundaries (from SEM) which supports the widely accepted IBL model, associated with MW polarization mechanism. The end result of this mechanism is the existence of semiconducting grains where the materials separated by insulating grain boundary barriers or other insulating interfaces.^{6–8} Adams *et al.*^{7,8} reported that coarse-grained (average grain size > 100 nm) CCTO ceramics sintered at 1100°C for 20 h showed a dielectric permittivity 2 orders of magnitude higher than fine-grained (average grain size: 5 nm) CCTO ceramics sintered at 1100°C for 3 h. Based on their complex impedance analysis, they explained that the high values of capacitance are attributed to ceramics with coarse grains forming a thin barrier layer at the grain boundaries^{7,8} as well as the presence of thin insulating second phase along with re-oxidized resistive layers near the grain boundaries was also considered as two possible reasons for high dielectric properties.^{7,8} According to the IBL model, the larger grain size creates the greater number of crystal defects than smaller ones, which allows for more internal barrier layers and leads to giant dielectric permittivity.^{9,25–28} However, IBL model could not fully explain the rapid suppression of high dielectric permittivity of CCTO at low temperatures and the large decrease in the dielectric permittivity value caused by chemical substitution at the A (=Ca) site of CCTO.¹⁵

CCTO1 ceramic samples have shown the lower values of the dielectric permittivity, when compared to CCTO2 ceramics, which can be attributed to the small grain size of CCTO1 ceramics sintered at 1050°C for 8 h. This may be due to the low sintering temperature and short duration of sintering for CCTO1 ceramics.⁹ However, it is also not ruled out that the presence of the small amount of CuO phase at the grain boundaries might be one more reason for high dielectric permittivity as reported in earlier literature.^{20–23,29} The only

drawback of these materials is high dielectric loss (not shown here); the increase in the dielectric loss is associated with an increase in the conductivity which is associated with an increase in the number of oxygen vacancies.⁹ These results are in agreement with energy-dispersive X-ray spectroscopy (EDX), which confirms the Cu rich content at the grain boundaries in CCTO pellets.

3.3. Impedance spectroscopy

Complex Impedance Spectroscopy (CIS) is a well known and powerful technique to describe the electrical properties of polycrystalline electro-ceramics. From CIS, bulk (contribution of grain-high frequency region), grain boundary contribution (low frequency region) [from Nyquist plots] and the effect of electrode specimen interface to the total resistance and capacitance, respectively, can be studied.^{18,30} In general, two distinct features — intragrain (bulk) and intergrain (grain boundary) — were shown in impedance spectrum. They are described in different complex plane formalisms. Imaginary component of impedance, Z'' , and electrical modulus, M'' , plotted against frequency data can give an effective way to investigate the electrical response of the materials.

The variation of imaginary (Z'') part of impedance with frequency at different temperatures is shown in Figs. 5(a) and 5(b) for CCTO1 and CCTO2 samples. Z'' values are higher in the low frequency region [Figs. 5(a) and 5(b)] and decrease monotonically with increase in frequency and remain invariant at higher frequencies. The imaginary part of impedance (Z'') attains a peak ($Z''_{\max}$) value and then decreases with frequency at all measured temperature from 30°C to 160°C (Figs. 5(a) and 5(b)). The non-existence of Z'' peak at all measured temperatures and frequencies in these ceramics is due to the absence of current dissipation in the material. For the two ceramic samples, the value of Z'' decreases with increase in frequency throughout the frequency range measured, indicating the capacitive behavior of the impedance. A decrease in Z'' magnitude with frequency

Fig. 5. Variation of imaginary impedance (Z'') and Electric modulus (M'') with frequency at different temperatures for CCTO1, CCTO2 ceramics pellets sintered at 1050°C (8 h) and 1100°C (30 h).

signifies the space charge polarization mechanism and their electrical behavior is frequency and temperature-dependent.³⁰ In higher temperature sintered [for longer time (30 h)] CCTO2 samples, the crystal size is increased with sharp crystal boundaries as shown in Fig. 5(b), resulting in the larger impedance for higher temperature sintered samples. Furthermore, Z'' decreases sharply in 1050°C sintered CCTO1 samples as compared to higher-temperature sintered CCTO2 sample which can be correlated with the charge carrier hopping mechanism.

Complex modulus formalism is an alternative approach to analyze the electrical properties of the materials. By utilizing complex modulus formalism, the presence of grain/grain boundary effect at elevated temperatures is evaluated. The electric modulus (M) is expressed as

$$M^* = M' + jM'' = j \times 2\pi f C_o Z^* = j \times 2\pi f C_o (Z' + jZ''),$$

where $C_o = \epsilon_o A/d$ is the geometrical capacitance, A is the electrode area and d is the distance between the electrodes.³⁰ Frequency dependence of imaginary part (M'') of electric modulus at different temperatures is shown in Figs. 5(c)–5(d). A temperature-dependent broadened peak maximum is observed in the lower frequency range (10^2 – 10^3 Hz). Its position

shifted towards high frequencies with increasing temperature indicating a thermally activated dielectric relaxation process in which the hopping mechanism of charge carriers dominates inherently.^{30,31} Frequency, dependent imaginary part M'' for both the samples also (Figs. 5(c) and 5(d)), shows a clear maximum at higher frequency region, with maxima shifting towards higher frequencies as the temperature increases, which is also a thermally-activated process. This maximum is associated with grain contribution.

Figure 6 shows the complex impedance spectrum (Z'' versus Z' , Nyquist plots) of CCTO1, CCTO2 ceramic samples measured at various temperatures in the frequency range from 100 Hz to 1 MHz. For the CCTO sintered pellets, the bulk semicircle near the origin (the intercept does not coincide with the origin from Fig. 6 inset) is not fully developed and took a straight line at high frequency region with large slope and low resistance values suggesting the semiconducting behavior. The bulk contribution to the impedance is predominant in the measured region. The grain contribution is considered as a parallel RC circuit. The low resistive impedance curves indicate the semiconducting nature of the ceramic sample. This semiconducting behavior may arise from a small amount of oxygen loss during ceramic

Fig. 6. Nyquist plots (Z' versus Z'') at selected temperatures for CCTO1, CCTO2 ceramics pellets sintered at 1050°C (8 h) and 1100°C (30 h).

processing in air at elevated temperatures.¹ Such behavior is also known to occur in other perovskite titanate-based materials.¹ Alternatively, intrinsic semiconductivity behavior is attributed to oxygen loss during ceramic processing in air at elevated temperature. Similar mechanism is also reported in structurally related $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ ceramics.³² It can also be seen that the Z'' maxima of the semicircle arc increase with decreasing of temperature. According to the IBLC theory,¹⁷ the current CCTO ceramics have shown that a straight line corresponds to the contribution of grains at high frequency and the partial semicircular arc behavior corresponds to the contribution of grain boundaries at low frequency, respectively.^{17,33,34} From Z'' versus Z' (Nyquist plots), as the sintering temperature and time increase, a significant decrease of the bulk resistance (R_b) is observed, similar results were also found in the literature.¹⁷ From the visual inspection of an enlarged view of Z'' versus Z' (Nyquist plots) for CCTO ceramics at high frequency region, given in Fig. 6 (inset), one can see that the complex plot is in the form of a straight line starting from the origin and then the semicircle arc is partially

formed with a large radius. The diameter of the semicircle and high frequency intercept on Z' -axis can approximately be regarded as grain boundary resistance (R_{gb}) and grain resistance (R_g), respectively, as shown in Table 2 at different temperatures. As the temperature increases, both grain and grain boundary resistances decrease for both CCTO ceramics. Low grain resistance in both of these ceramics is attributed to semiconducting nature at all measured temperatures.

The straight line, which indicates the resistive behavior at higher-frequency region which contributes to the one resistance element in a parallel equivalent R-C circuit, due to grain contribution. As well a non-zero intercept of the data on the real Z' axis. Bulk semicircular arc size decreasing with increasing temperature is attributed to be of thermally activated charge transport.¹⁷ Here we conclude that the appearance of partial semicircular arc both at high and low temperatures is due the bulk (grain) property of material. Figure 7 shows the complex electric modulus spectrum (M' versus M'') of CCTO1, CCTO2 ceramic samples measured at various

Table 2. Impedance parameters (grain resistance R_g , grainboundary resistance R_{gb}) of the CCTO1, CCTO2 samples at different temperature (30°C-160°C).

Temperature (°C)	Grain resistance (R_g)-(8H) (ohm)	Grain boundary resistance (R_{gb})-(8H) (k-ohm)	Grain resistance (R_g)-(30H) (ohm)	Grain boundary resistance (R_{gb})-(30H) (k-ohm)
30	240	868	102	4031
40	230	817	100	3980
50	234	754	970	3796
60	232	720	965	3656
70	231	701	910	3421
80	227	635	906	3264
90	225	620	872	2859
100	222	595	858	2554
110	220	562	834	2198
120	215	514	809	1784
130	214	496	782	1400
140	207	426	788	1068
150	204	412	722	714
160	202	384	690	653

Fig. 7. Electric modulus plots (M' versus M'') at selected temperatures for CCTO1, CCTO2 ceramics pellets sintered at 1050°C (8 h) and 1100°C (30 h).

temperatures in the frequency range from 100 Hz to 1 MHz. Modulus analysis of these ceramics confirms the presence of temperature-dependent MW polarization relaxation mechanism at all measured temperatures and frequencies.³⁵ From complex electric modulus plots, a single semicircular arc is observed at high frequency followed by a straight line tail at low frequency at all measured temperatures. This semicircular arc at high frequency is attributed to bulk or grain part of the material, which shows the capacitance contribution.

The frequency dependence of the ac conductivity (σ_{ac} in log-log scale) at different temperatures is shown in Fig. 8. The σ_{ac} can be expressed in terms of the permittivity (ϵ_r) and the dissipation factor ($\tan \delta$):

$$\sigma_{ac} = \omega \epsilon_r \epsilon_0 \tan \delta,$$

where $\omega (= 2\pi f)$ is the angular frequency and ϵ_0 is permittivity of free-space or vacuum.

The conductivity for the two samples is found to increase with increasing frequency. It is also revealed from the conductivity measurements, as the temperature increased from room temperature to 160°C, conductivity is slightly increased

with sintering time. The CCTO2 pellet conductivities show a dispersion pattern at low frequency with increasing temperature. However, there is not much variation in the conductivity at higher frequency region for both pellets. At low frequency, moderately flat response of the conductivity is attributed to the σ_{dc} part of the conductivity. It is concluded that the conductivity (σ_{ac}) increases with increasing sintering temperature and time. This increase in conductivity with temperature is due to the semiconducting behavior of the ceramics. The main feature of this plot is the appearance of σ_{dc} in the low frequency ($< 10^4$ Hz) region and σ_{ac} in the ($> 10^4$ Hz) high-frequency regions, and hence showing a change in slope at a particular frequency. And the frequency at which the slope changes is known as hopping frequency. At low frequency, moderately flat response of the conductivity is attributed to the σ_{dc} part of the conductivity. It is concluded that the conductivity (σ_{ac}) increases with increasing sintering temperature and time.⁹ According to Kröger-Vink defect notation, during sintering process, oxygen vacancies were formed due to loss of the oxygen.^{35,36} Upon cooling, insulating grain boundaries re-oxidize faster (grain boundary diffusion) than that of semiconducting grain

Fig. 8. Variation of ac conductivity as a function of frequency at selected temperatures for CCTO1, CCTO2 ceramics pellets sintered at 1050°C (8 h) and 1100°C (30 h).

interiors, which in turn prevents the degradation of the enhanced conductivity of the grains, leading to the formation of a giant dielectric IBLC-like perovskite behavior.⁹ In ABO₃ type perovskite, both grains and grain boundary resistivity values are different due to equilibrium concentration of oxygen vacancies, which results in loss of oxygen during sintering process. This linear increase in σ_{ac} relates to the electrical conduction by electron exchange between ($\text{Cu}^{+2} \leftrightarrow \text{Cu}^{+1}$) the Cu ions with different valence (Cu^{+2} and Cu^{+1}) states.^{35–37} The electrons released in the above reaction were captured by the Cu^{+2} to form Cu^{+1} ($\text{Cu}^{+}\bullet$). This leads to hopping of electrons among the two different valence states, which increases the conductivity of the grains.^{35–37} However, in case of stoichiometric CCTO, the conduction mechanism is attributed to the hopping of the charge carriers between the Cu^{2+} and Cu^{3+} .²⁹

3.4. Conclusions

In this study, we investigated the effect of dielectric properties of the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics prepared by sol–gel synthesis method at different sintering temperatures for different sintering times (1050°C after 8 h and 1100°C after 30 h). A major CCTO phase was identified for both ceramics, besides the minor phases of TiO_2 and CuO . The microstructures of the ceramics show an abnormal grain growth for 30 h sintered ceramics. The average grain size of CCTO was increased with increasing sintering time. CCTO ceramics have shown marked microstructural variation as a result of abnormal grain growth, which again considerably alters the dielectric properties. The segregation of CuO at grain boundary, formation of oxygen vacancies, and the aliovalences of Cu and Ti ions in CCTO lattice are considered to play important roles in evolution of the IBLC structure of semiconducting grains (domains) and insulating grain boundaries in CCTO ceramics along with MW polarization mechanism which is well pronounced in these CCTO ceramic pellets. The dielectric permittivity measurement shows that the ϵ is increased with increasing sintering temperature and sintering time. Enhanced dielectric permittivity in these CCTO ceramics is ascribed to the IBLC model associated with MW polarization mechanism. Temperature-dependent impedance and modulus analyses of these ceramics with one semicircular arc were proved to confirm the bulk property of the materials.

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