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DEVELOPMENT OF DIELECTRIC MATERIAL, $CaCu_3Ti_4O_{12}$

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ABSTRACT

$CaCu_3Ti_4O_{12}$ (CCTO) was prepared by a conventional solid state reaction method. CCTO sample was pre-sintered at 900°C for 10 hours and sintered at 1075°C for 12 hours. The dielectric properties of the sample were measured using HP 4192A LF Impedance Analyzer. The complex permittivity was measured within the frequency range from 10 Hz to 10^6 Hz and the temperature ranging from 30°C to 400°C. The results showed that the dielectric constant and dielectric loss factor of the sample are frequency dependent and temperature dependent. CCTO sample exhibits a high dielectric constant which is around 10^5. Dielectric constant increases with decreasing frequency due to interfacial polarization. This could be explained by the Maxwell-Wagner effect.

INTRODUCTION

$CaCu_3Ti_4O_{12}$ was first synthesized by Bochu et al. [1]. It has been reported that single crystal, ceramic and thin film of CCTO [1-5] have attracted much interest due to its unusually high dielectric constant $\varepsilon \sim 10^4$ at low frequencies which remains almost constant between 100 and 600 K [1-3,5-11].

The original work done by Subramanian et al. and Ramirez et al. showed that room temperature permittivity were from 10,000 to 20,000 [9] making it ideal for a wide range of applications. Recently, researchers claim that this behaviour comes from different factors, such as grain boundary, the presence of twin boundaries or other planar defects, displacement of Ti ions, etc. [1,2,4,6,8-10,12-14]. But, the nature of how the CCTO represents such properties and the real explanations of the phenomena are still investigated. At present, the grain boundary barrier layer capacitance model of extrinsic mechanism is the most favourable one. The insulating layers are thought to cause internal boundary layer capacitance (IBLC). The IBLC model was recently supported by different observations of defects inside both single crystals and grains of polycrystalline CCTO and by complex impedance spectroscopy measurements on a CCTO crystal [1,2,6,9,11,15].

Besides, the dielectric properties of CCTO ceramics are very sensitive to processing [1,2,5,9,11]. This paper reports the results of the dielectric measurement on CCTO ceramics sintered at 1075°C at various temperatures from 30°C to 400°C.

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EXPERIMENTAL METHOD

The CCTO ceramic was produced using the conventional solid state reaction method. CaO (99.95% purity), CuO (99.9% purity), and TiO_2 (99.7% purity) were used as starting materials. Stoichiometric amounts were weighed and mixed by ball milling for 24 hours. The powder was calcined in air at 900°C for 10 hours. The powder was put in a Planetary Micro Mill to grind for 6 hours to ensure the particles sizes of the powder are sufficiently homogeneous. After the sieving process, the powder was granulated by adding 2% polyvinyl alcohol (PVA) as a binder. The powder was pressed manually by Hydraulic Presser to mould the pellet shape. The pellet was sintered at 1075°C for 12 hours and then cooled to room temperature in the furnace.

The crystal structures of the sample were examined by X-ray diffraction (XRD). The dielectric properties of the sample were determined using the HP 4192A LF Impedance Analyzer in the frequency range from 10 Hz to 10^6 Hz at 30°C and 50°C – 400°C at 50°C intervals.

RESULTS AND DISCUSSION

Table 1 shows the values of the dielectric constant and dielectric loss for CCTO measured at 30°C to 400°C. From the data, the values of both dielectric constant and dielectric loss increase as temperature increases. However, as frequency increases, the dielectric constant and dielectric loss decrease.

Table 1: Dielectric constant and dielectric loss for CCTO measured at different temperatures

Temperature (°C)	Frequency (Hz) 100		1000		10000		100000	
	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
30	1.77E+02	4.38E+02	1.39E+02	6.60E+01	1.23E+02	9.39E+00	1.20E+02	1.60E+00
50	1.81E+02	4.05E+02	1.40E+02	6.90E+01	1.21E+02	9.80E+00	1.19E+02	1.37E+00
100	2.18E+02	4.76E+02	1.84E+02	7.93E+01	1.33E+02	2.60E+01	1.21E+02	4.32E+00
150	4.43E+02	7.42E+02	2.34E+02	1.49E+02	1.65E+02	4.47E+01	1.34E+02	1.81E+01
200	6.95E+02	4.95E+03	4.32E+02	6.23E+02	2.38E+02	1.51E+02	1.54E+02	3.50E+01
250	7.15E+02	3.40E+04	3.99E+02	3.49E+03	3.09E+02	4.02E+02	1.98E+02	9.55E+01
300	1.08E+03	1.86E+05	4.59E+02	1.88E+04	3.11E+02	1.94E+03	2.56E+02	2.41E+02
350	2.44E+03	8.19E+05	5.67E+02	8.23E+04	3.29E+02	8.30E+03	2.65E+02	8.57E+02
400	6.95E+03	2.09E+06	9.90E+02	2.10E+05	2.51E+02	2.10E+04	2.15E+02	2.13E+03

Figures 1 and 2 represent the permittivity for CCTO ceramics variation with temperature and frequency. The sample exhibits giant permittivity at low frequency for 300°C, 350°C, and 400°C. As frequency increases, permittivity drastically decreases and approaching a constant value at 1 MHz. The increment of permittivity as frequency decreases could possibly be due to interfacial polarization. The charge carriers may be blocked at the electrode interface under the influence of an electric field [9]. It has been reported that CCTO ceramics consist of insulating grain boundaries and semi-conducting grains. The charge carriers accumulated at the interface between semiconducting grains and insulating grain boundaries resulted in an increase in the dielectric constant [5]. This is the famous Maxwell-Wagner effect [6,9].

Dielectric loss factor of the sample exhibits dc conduction losses. It shows the dielectric loss of CCTO drastically decreases with increasing frequency. The dielectric loss increases with temperature from 30°C to 400°C. The frequency and temperature effect on the dielectric loss illustrates the interfacial polarization of the grain boundaries within the sample. These frequency and temperature dependence are due to the conversion of the movement of phonons into the vibrations of the lattice. The inconsistent lattice vibrations cause instability in the interfacial polarization. Therefore, the dielectric loss increases.

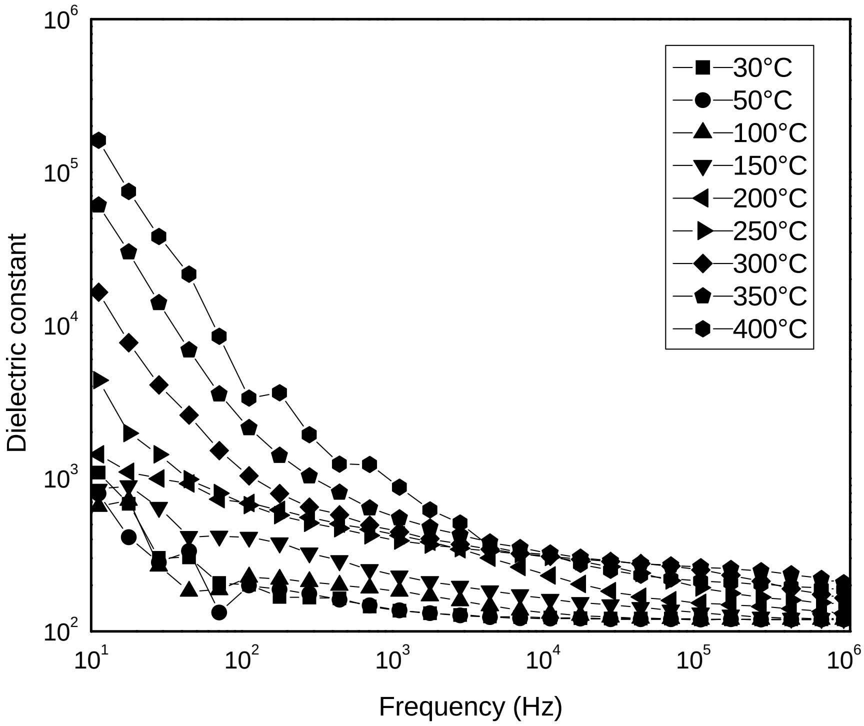

Figure 1: Dielectric constant of CCTO measured at different temperatures

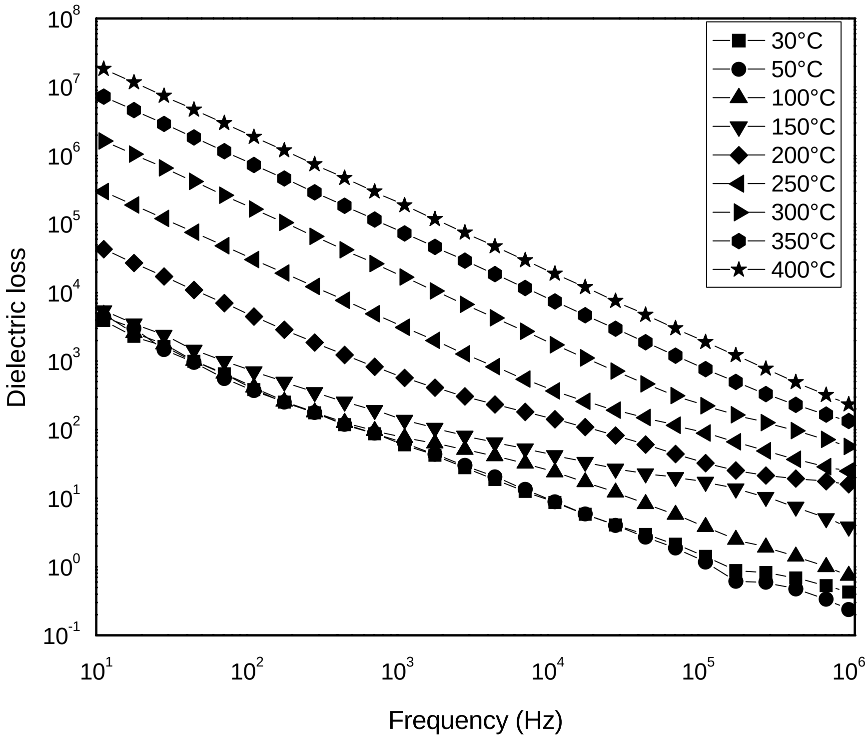

Figure 2: Dielectric loss of CCTO measured at different temperatures

The dielectric constants of CCTO at selected frequencies such as 10^2 Hz, 10^3 Hz, 10^4 Hz and 10^5 Hz with respect to temperature (30°C – 400°C) are given in Figure 3. It exhibits the temperature dependence of CCTO. The dielectric constant of CCTO increases with increasing temperature. The increment of dielectric constant is low from 30°C – 250°C especially during higher frequencies. This means that there exists mechanical limitation where lack of interfacial polarization occurs at higher frequencies. There results in a large variation between 300°C – 400°C at low frequencies due to the increase in interfacial polarization. Figure 4 shows the dependence of CCTO with temperature. Dielectric loss drastically increases as the temperature increases.

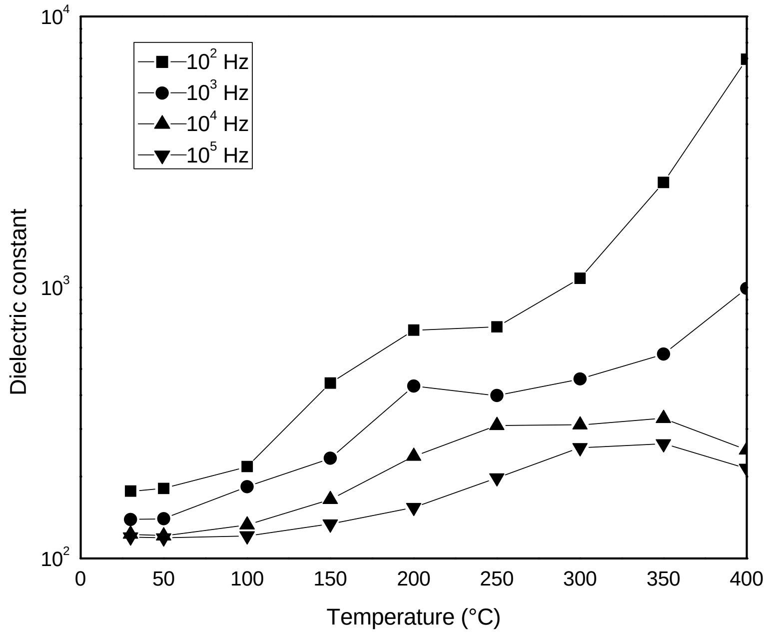

Figure 3: Dielectric constant of CCTO with respect to temperature at selected frequencies

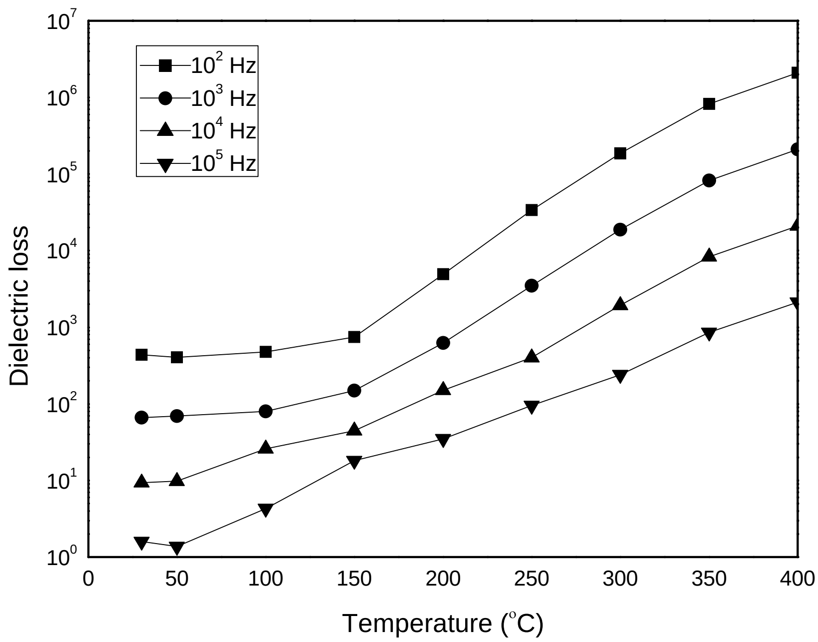

Figure 4: Dielectric loss of CCTO with respect to temperature at selected frequencies

CONCLUSION

According to experimental results, CCTO with high dielectric constant was successfully prepared via conventional solid state reaction method. The dielectric properties of CCTO ceramic are very sensitive to processing. The dielectric constant and dielectric loss decrease with an increase in frequency. The dielectric constant and dielectric loss increase with an increase in temperature.

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