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AC CONDUCTIVITY OF $Ca_{1-x}A_xCu_3Ti_4O_{12}$ (A = Sr or Ba) with x = 0.0 and 0.2 CERAMICS

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ABSTRACT

Colossal dielectric constant materials such $CaCu_3Ti_4O_{12}$ (CCTO) have recently received an enormous of attention because of their potential in technological applications due to the formation of internal barrier layer capacitor (IBLC) contains semiconducting grains with insulating grain boundaries. $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ (CSCTO) and $Ca_{1-x}Ba_xCu_3Ti_4O_{12}$ (CBCTO) with x = 0.0 and 0.2 ceramics has been doped on Ca site with strontium or barium was prepared using solid state reaction technique. X-ray diffraction pattern shows single phase with cubic structure. In complex impedance plot for both the ceramics show three semicircular arcs represent the grain, the grain boundary and electrode effect responses and modeled using series network of three parallel RC circuits. Two regions were found in conductivity plot due to the grain boundary at low frequencies and the grain at high frequencies. The n value obtained from the fitting at the grain region at high frequency dependent are above 0.6 indicates of electron hopping conduction mechanism among Ti^{3+} and Ti^{4+}. The activation energy values for CCTO are 0.28 eV and 0.74 eV for grain and grain boundary regions, respectively while for CSCTO the energies is 0.27 eV and 0.71 and for CBCTO is 0.31 eV and 0.59 eV for the grain and grain boundary regions respectively.

INTRODUCTION

$CaCu_3Ti_4O_{12}$ (CCTO) has attracted an attention based on its extraordinary dielectric properties and makes it applicable to a microelectronic device application for capacitive element. The $ACu_3Ti_4O_{12}$ family of compounds has been known since 1967 and most exceptional behavior is exhibited by $CaCu_3Ti_4O_{12}$ (CCTO) ceramics which is first synthesized by Bochu *et al.* [1]. CCTO with cubic perovskite structure of space group *Im*-3 shows a giant dielectric response and has extremely high value of dielectric constant ε' about 10,000 at 1 kHz [2]. Based on impedance spectroscopy (IS), high permittivity is associated to an “extrinsic” effect due to an internal barrier layer capacitance (IBLC) consist of insulating grain boundaries and semiconducting grains [3]. It was reported that most composition $A_{2/3}Cu_3Ti_4O_{12}$ (A = trivalent rare earth) shows dielectric constants above 1000 at 100 kHz. Those of the composition $ACu_3Ti_4O_{12}$ (A = Ca, Sr and Ba) show dielectric constant above 1000 except for $BaCu_3Ti_4O_{12}$ where the value is below 1000 [4]. In this paper, we study the ac conductivity of CCTO, $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ (CSCTO) and $Ca_{1-x}Ba_xCu_3Ti_4O_{12}$ (CBCTO).

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METHODOLOGY

CCTO, CSCTO and CBCTO ceramics was prepared by solid state reaction technique. Stoichiometric amounts of high purity calcium carbonate, strontium carbonate, barium carbonate, titanium dioxide and copper (II) oxide were weighed and mixed in an agate mortar and pestle. The mixture was calcined in alumina crucible at 900 ^{o}C for 10 hours. The powder was reground for 2 hours and pressed into pellets. Both powders and pellets were sintered in air at 1050 ^{o}C for 24 hours.

XRD was done on sintered powders to monitor phase evolution using Pan Analytical (Model Philips PW3040). Microstructural characterization of the ceramic was carried out by scanning electron microscope (SEM) (Model Hitachi TM0603). Sintered pellets were polished to achieve smooth and parallel surfaces and were sputtered with silver as electrodes using RF Magnetron Sputtering. The AC measurement was done from 30 to 250 ^{o}C in frequency range of 10^{-2} to 10^{6} Hz using High Dielectric Resolution Analyzer (Novocontrol Novotherm).

RESULTS AND DISCUSSION

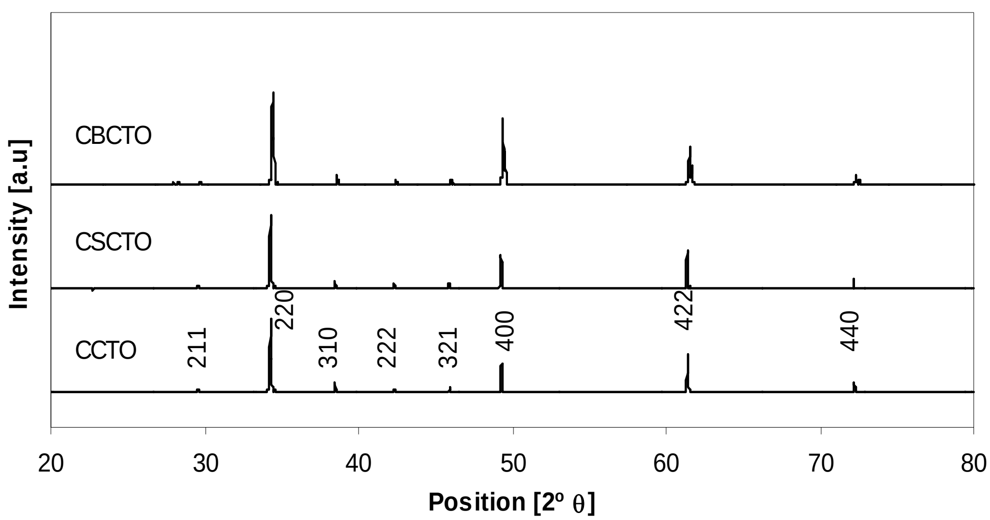

Figure 1: X-ray diffraction patterns of CCTO, CSCTO and CBCTO.

Figure 1 shows the x-ray diffraction patterns of CCTO, CSCTO and CBCTO with cubic structure and calculated lattice parameter ’a’ = 7.3870 Å, 7.3935 Å and 7.3993 Å respectively. The lattice parameter increase as Sr^{2+} or Ba^{2+} ions replace the Ca^{2+} ion in CCTO. The values of lattice parameter for CBCTO are much higher than CSCTO and CCTO since the ionic radius of Ba^{2+} (1.34 Å) is higher than Sr^{2+} (1.12 Å) and Ca^{2+} (0.99 Å). Figure 2 shows SEM images of the surface morphology of CCTO, CSCTO and CBCTO ceramics. The morphology shows the grain and grain boundary for all the ceramics. The grain size is dependent with the doping ions where the doping of Sr^{2+} or Ba^{2+} on Ca^{2+} ions increases the grain size.

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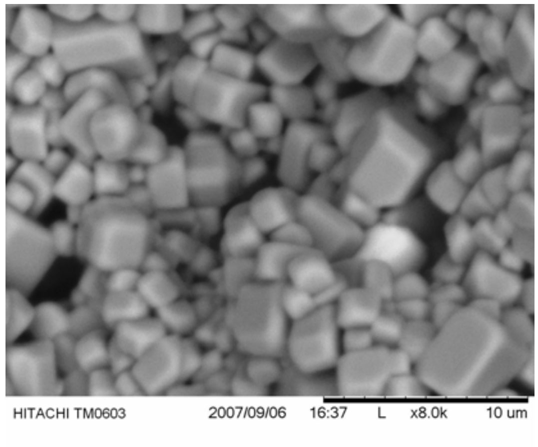
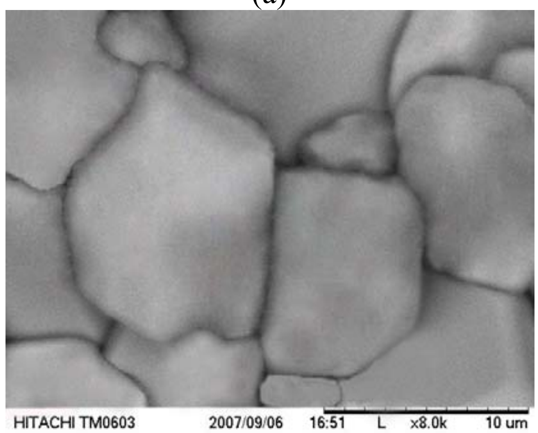
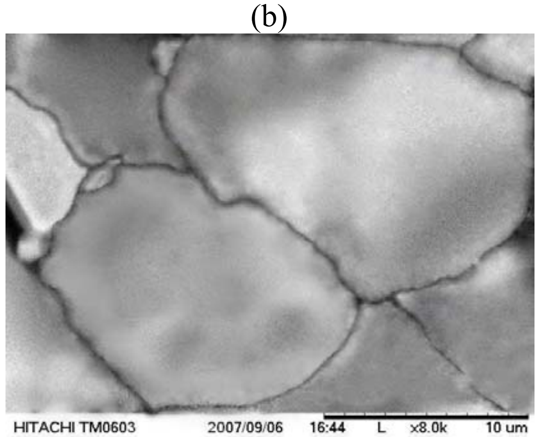


(a)



(b)



(c)

Figure 2: Electron micrograph for (a) CCTO, (b) CSCTO and (c) CBCTO consist of grain and grain boundary.

Figure 3 (a) shows the complex impedance, Z^* plot for CCTO at 230, 210, and 190 ^oC which consists of three semicircle arcs with centre below the Z' axis. The semicircle arc

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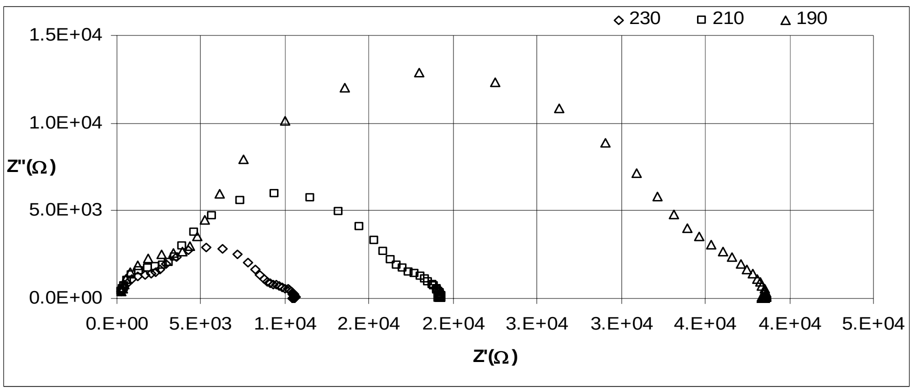
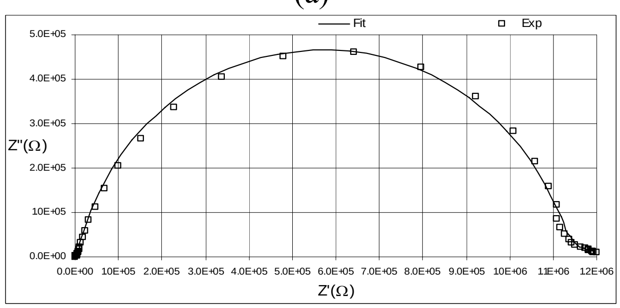
at high frequency is due to the grain, at middle frequency is due to grain boundary while at low frequency is attributed to electrode effect. Figure 3 (b) and (c) shows the complex impedance for CSCTO and CBCTO at 210 ^oC with fitted curve using three parallel resistors and the universal capacitor connected in series. For CSCTO the grain semicircle arc at high frequency has been suppressed due to the high value of grain boundary resistance usually observed for internal barrier layer capacitance (IBLC) due to the characteristic of semiconducting grain with insulating grain boundary [5]. For CBCTO, the complex impedance show overlapped semicircle arcs between the grain and grain boundaries and a small semicircle arc at low frequency due to electrode effect. The overlapped semicircle arcs between the grain and grain boundary is maybe due to the melted grain and the formation of not well defined boundaries.



(a)



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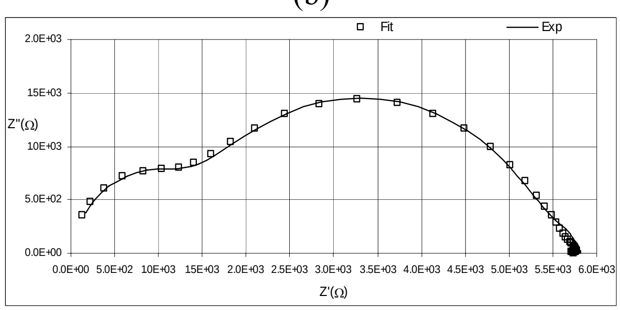

(c)

Figure 3: Complex impedance plot of polycrystalline (a) CCTO at 230, 210, and 190 ^oC (b) CSCTO and (c) CBCTO at 210 ^oC with fitted curve using equivalent electrical circuit.

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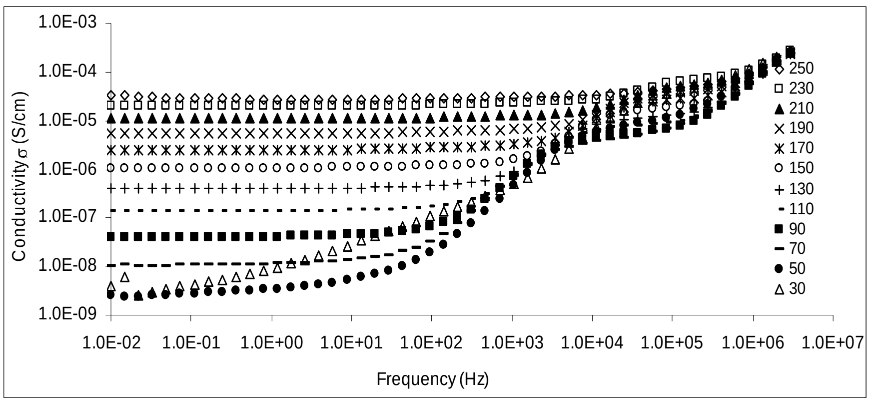
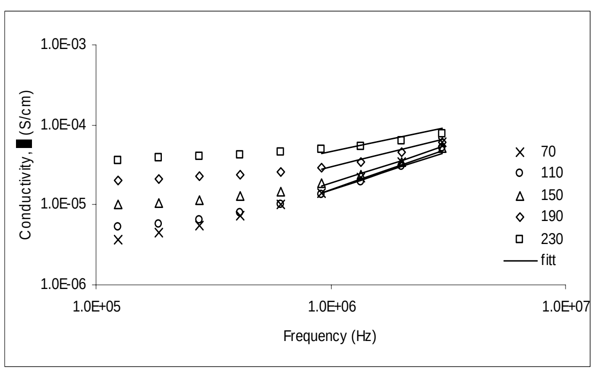
Figure 4(a) shows the conductivity versus frequency for CCTO at 30 ^oC to 250 ^oC and there are two regions due to grain boundaries at low frequency and at high frequency attributed to the grain. The rise in value of conductivity with temperature indicates that the electrical conduction in the material is a thermally activated process. The conductivity for CCTO, CSCTO and CBCTO was fitted at grain region at high frequency dependent as showed in Figure 4(b) and (c) respectively for CSCTO and CBCTO. The equation can be expressed as

$$\sigma(\omega) = A\omega^n \quad (1)$$

in which ω is the angular frequency, A determines the magnitude of the dispersion found at high frequencies and n is an exponent lies in the range 0 to 1. The value of n obtained from fitting was above 0.6 and decreases with increase temperatures indicating that the conduction is due to hopping process of electrons between Ti^{4+} and Ti^{3+} [6].



(a)



(b)

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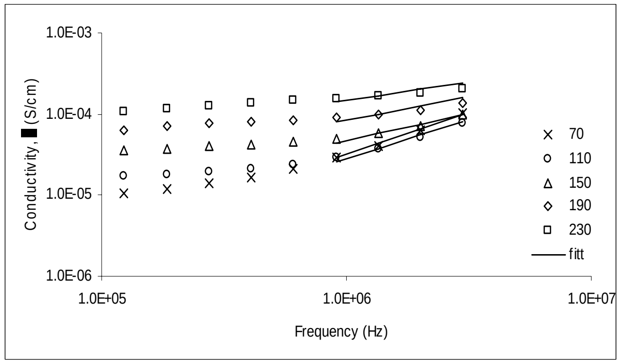

(c)

Figure 4: (a) Conductivity of CCTO at 30 °C to 250 °C and high frequency dependent fitting for (b) CSCTO and (c) CBCTO from 70 °C to 230 °C.

The grain conductivity (σ_g) and the grain boundary conductivity (σ_{gb}) was calculated in term of the grain resistance (R_g) and the grain boundary resistance (R_{gb}) evaluated from complex impedance fitting with the relation $\sigma = d/RA$ where *d* is thickness and *A* is the area. The conductivity σ follows the Arrhenius law and which is described by the expression

$$\sigma = \sigma_o \exp(-E_a/kT) \quad (2)$$

where E_a is the activation energy and *k* is the Bolzmann's constant. The activation energies of σ_g and σ_{gb} were found from the slopes of Arrhenius plot show in Figure 5 and the values were listed in Table1.

Figure 5: Arrhenius plot of CCTO for the grain and grain boundary regions.

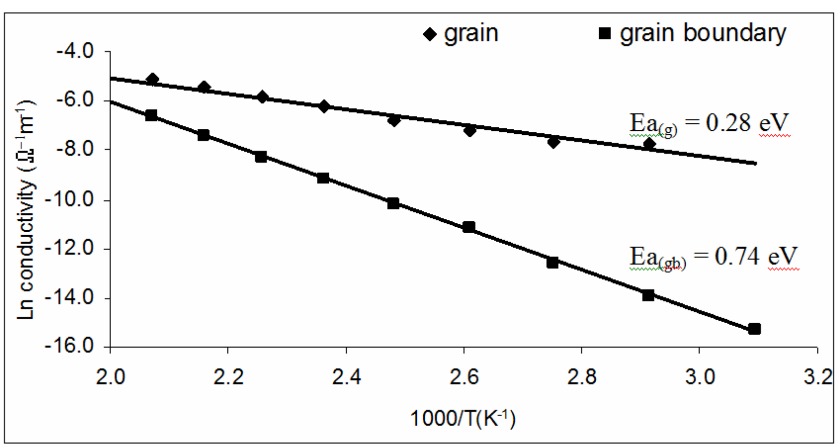

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Table1: The values of activation energies for CCTO, CSCTO and CBCTO for the grain and grain boundary region.

Samples	**Activation Energy (eV)**	
	$Ea_{(g)}$	**$Ea_{(gb)}$**
CCTO	0.28	0.74
CSCTO	0.27	0.71
CBCTO	0.31	0.59

CONCLUSION

The XRD pattern for CCTO, CSCTO and CBCTO shows cubic structure with calculated lattice parameter 'a' = 7.3870 Å, 7.3935 Å and 7.3993 Å respectively increase as the ionic radius of doping ions increase. The complex impedance show three responses due to the grain effect at high frequency, the grain boundary at middle frequency and electrode effect at low frequency. The conductivity plots show two regions attributed to grain boundary and grain at low and high frequency respectively. The activation energy values for CCTO are 0.28 eV and 0.74 eV for grain and grain boundary regions, respectively while for CSCTO the energies is 0.27 eV and 0.71 and for CBCTO is 0.31 eV and 0.59 eV for the grain and grain boundary regions respectively.

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