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IMPEDANCE SPECTROSCOPY ON HIGH DIELECTRIC PERMITTIVITY OF $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ CERAMIC SAMPLES

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ABSTRACT

$Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ (x = 0.0, 0.1, 0.5) ceramics has been doped on Ca site with strontium using solid state reaction technique. Impedance measurement was done from 30 ^oC to 250 ^oC in frequency range of 10^{-2} Hz to 10^6 Hz. X-ray diffraction pattern shows single phase for all samples, while cubic structure with lattice parameter a = 7.3870Å is obtained for undoped sample. In complex impedance plot, three semicircular arcs represent electrode effect, grain boundary and bulk responses are observed. The results ware fitted using series network of three parallel RC circuits. The value of resistance is increasing while the value of capacitance has minor changes when temperature decreased. From Arrhenius plot of resistivity data for x = 0.1, the activation energy, E_a are 0.145 eV and 0.320 eV for bulk and grain boundary regions, respectively. Meanwhile, the E_a value for x = 0.5 are 0.137 eV for bulk regions, and 0.464 eV for grain boundary regions.

INTRODUCTION

A colossal dielectric constant (CDC) material are widely investigated for their unique property and is very promising for capacitor applications and certainly for microelectronics and microwave devices where the miniaturization of devices is crucial [1]. 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. CCTO has cubic perovskite structure with space group *Im*-3. CCTO shows a giant dielectric response and has extremely high value of dielectric constant ε' at 1 kHz of about 10,000. [2]. Based on impedance spectroscopy (IS), high permittivity is associated to an "extrinsic" effect due to an internal barrier layer capacitance (IBLC) effect where insulating surfaces or grain boundaries form on semiconducting grains during processing of CCTO ceramics [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].

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THEORY

The frequency dependent properties of a material can be describe via four possible complex formalisms; the complex permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$), complex impedance ($Z^* = Z' - iZ''$), complex admittance ($Y^* = Y' + iY''$), and complex electric modulus ($M^* = M' + iM''$). The above formalisms are interrelated as:

$$\varepsilon^* = \frac{1}{i\omega Z^* C_o} = \frac{Y^*}{i\omega C_o} = \frac{1}{M^*}$$

where $C_o = \varepsilon_o A/d$, A is area, d is thickness of the sample, ω is angular frequency (2πf) and $\varepsilon_o = 8.854 \times 10^{-14}$ Fcm^{-1} is permittivity of free space.
Circuit that consists of parallel R (resistance) and C (capacitance) which connected in series represents grain boundary and bulk response. One parallel RC elements produce one semicircle in complex impedance plot as shown in Figure 1.

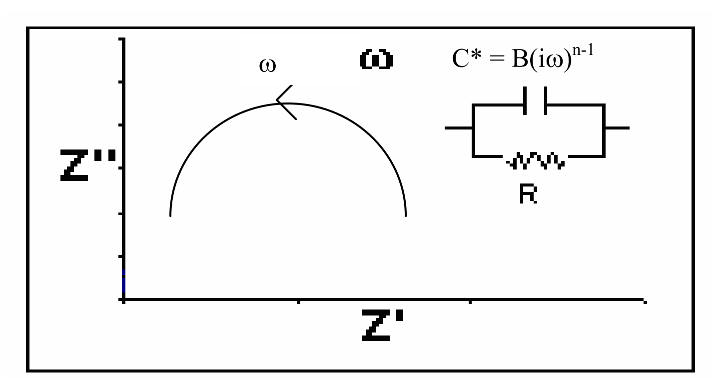

Figure 1: Complex impedance plot (Z'' vs. Z') for parallel RC circuit.

The complex impedance plot was fitted using universal capacitor $C^* = B(i\omega)^{n-1} = \frac{1}{R}\left(\frac{\omega}{\omega_p}\right)^{n-1}\left(\sin\frac{n\pi}{2} - i\cos\frac{n\pi}{2}\right)$, where the real and imaginary part of impedance can be written as

$$Z' = \frac{\frac{1}{R}\left[1 + \left(\frac{\omega}{\omega_p}\right)^n \cos\frac{n\pi}{2}\right]}{\left[\frac{1}{R}\left(1 + \left(\frac{\omega}{\omega_p}\right)^n \cos\frac{n\pi}{2}\right)\right]^2 + \left[\frac{1}{R}\left(\left(\frac{\omega}{\omega_p}\right)^n \sin\frac{n\pi}{2}\right)\right]^2}$$

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$$Z''=\frac{\frac{1}{R}\left[\left(\frac{\omega}{\omega_p}\right)^n \sin\frac{n\pi}{2}\right]}{\left[\frac{1}{R}\left(1+\left(\frac{\omega}{\omega_p}\right)^n \cos\frac{n\pi}{2}\right)\right]^2+\left[\frac{1}{R}\left(\left(\frac{\omega}{\omega_p}\right)^n \sin\frac{n\pi}{2}\right)\right]^2}$$

where B is constant, n value lies in the range ($0 < n < 1$) and R is resistance.
The resistivity ρ is calculated using $\rho = R\,A/d$ where R is a Resistance value from fitting results, A is area and d is the distance. The conductivity σ is calculated using resistivity data by equation $\sigma = 1/\rho$. The conductivity σ follows the Arrhenius law and can be described by the expression

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

where E_a is the activation energy and k is the Bolzmann's constant.

EXPERIMENTAL PROCEDURE

$Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ (x = 0.0, 0.1, 0.5) ceramics were prepared using solid state reaction technique using raw materials such as calcium carbonate ($CaCO_3$)**,** strontium carbonate ($SrCO_3$), titanium dioxide (TiO_2) and copper (II) oxide (CuO). The materials were weighted according to the stoichiometric ratios and were ground for 3 hours. The mixed powders were calcined at 900 ^oC for 10 hours. The calcined powders were regrinded for 2 hours to improve its homogeneity before sintered in air at 1050 ^oC for 24 hours in powders and pellet form. XRD (Philips Model PW3040) was done on sintered powders to monitor phase evolution using. Sintered pellets were polished to achieve flat and parallel surfaces and were sputtered with silver as electrode using RF Magnetron Sputtering. Impedance measurement was done from 30 ^oC to 250 ^oC in frequency range of 10^{-2} Hz to 10^6 Hz using Novocontrol Novotherm High Dielectric Resolution Analyzer.

RESULTS AND DISCUSSION

XRD patterns for $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ with x = 0.0, 0.1, 0.5 are shown in Figure 2. The patterns show single phase for all samples, while cubic structure with calculated lattice parameter a = 7.3870 Å for undoped sample compared to 7.3590 Å as reported by P. Jha *et al.* [5].

Figure 3 shows complex impedance plots for $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ (x = 0.1 and 0.5) at 190 ^oC, 210 ^oC and 230 ^oC. The graphs show three semicircular arcs. The semicircle at high frequency is attributed to the bulk properties while the second semicircle represents grain boundary properties. The third semicircle at low frequency is due to

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electrode effects. It is obvious that the value of resistance increases as the temperature decreases. The presence of three semicircular arcs can be modeled as an equivalent electrical circuit comprising of the combination of series network of three parallel RC circuits and series resistor, Rs as shown in Figure 4. The fitting parameters for x = 0.1 are listed in Table 1.

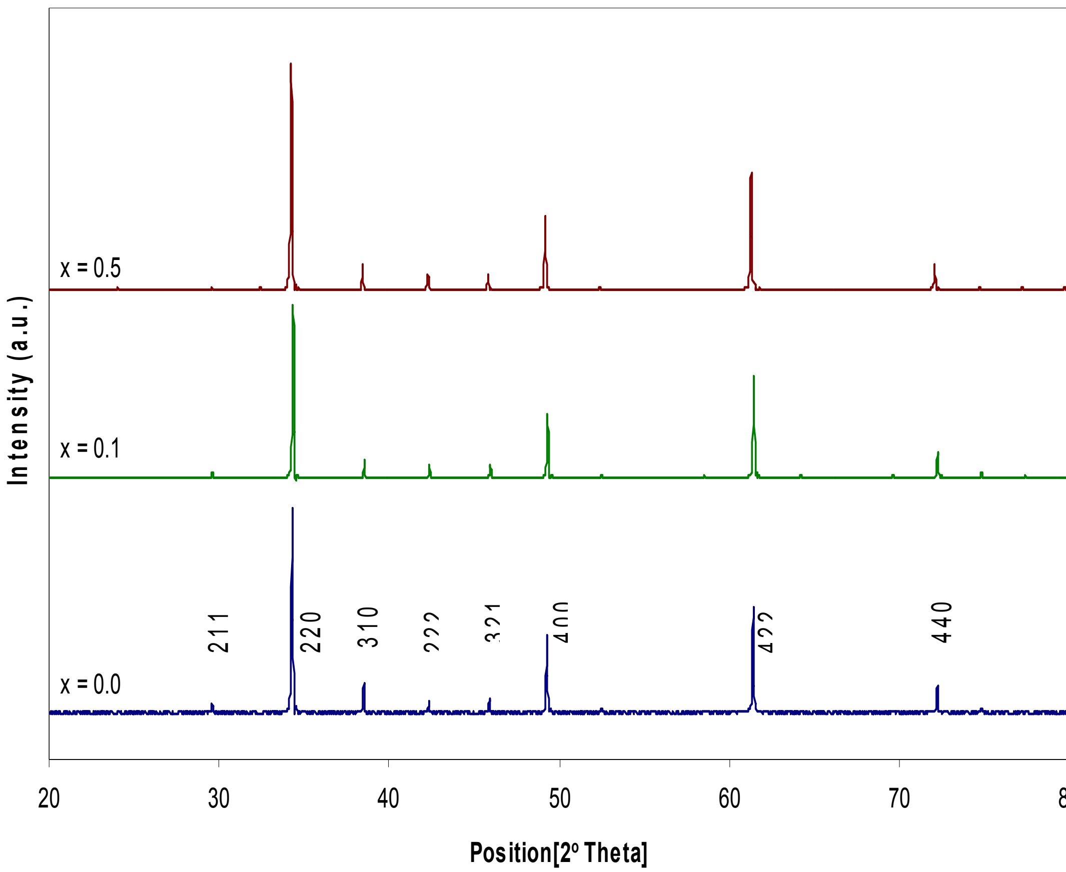

Figure 2: X-ray diffraction patterns of $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ (x = 0.0, 0.1, 0.5)

Figure 5 shows the conductivities of bulk and grain boundary layers of the samples against reciprocal temperature. The activation energy value for x = 0.1 are 0.145 eV and 0.320 eV for bulk and grain boundary regions, respectively. While the E_a value for x = 0.5 are 0.137 eV for the bulk regions, and 0.464 eV for grain boundary regions.

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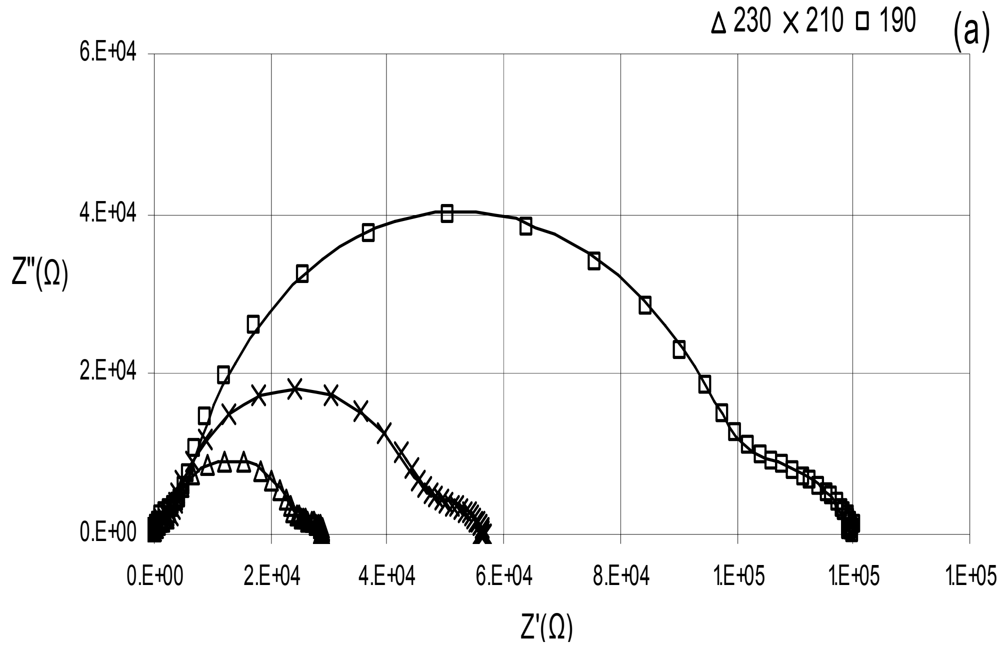
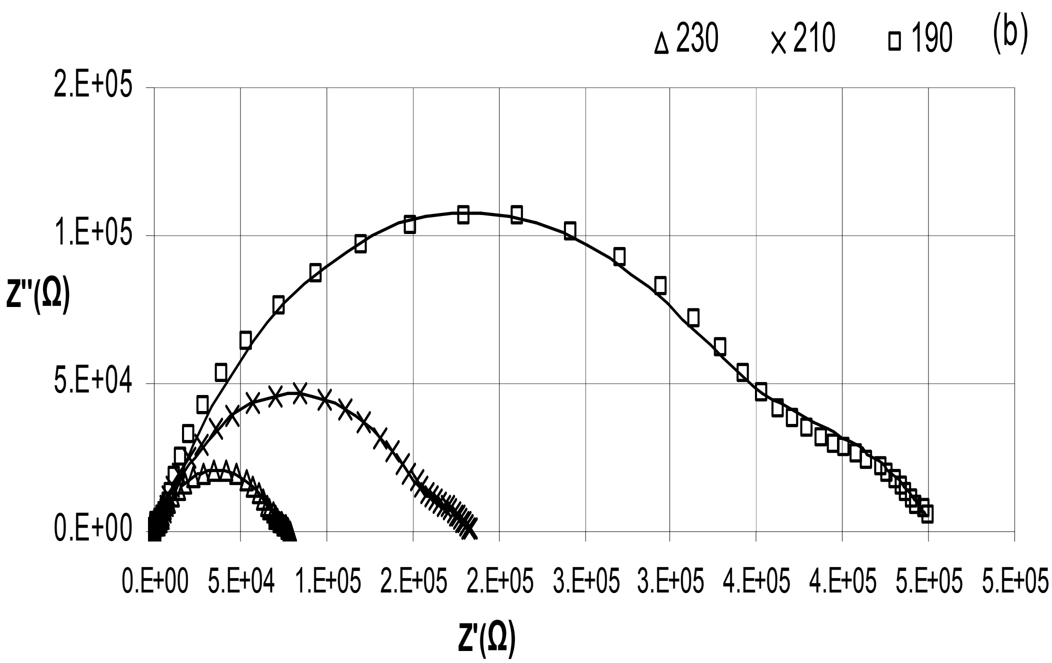


(a)



(b)

Figure 3: Selected complex impedance plots of $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ ceramics with fitting using equivalent circuits for (a) x= 0.1 (b) x = 0.5 at 190°C, 210°C and 230°C.

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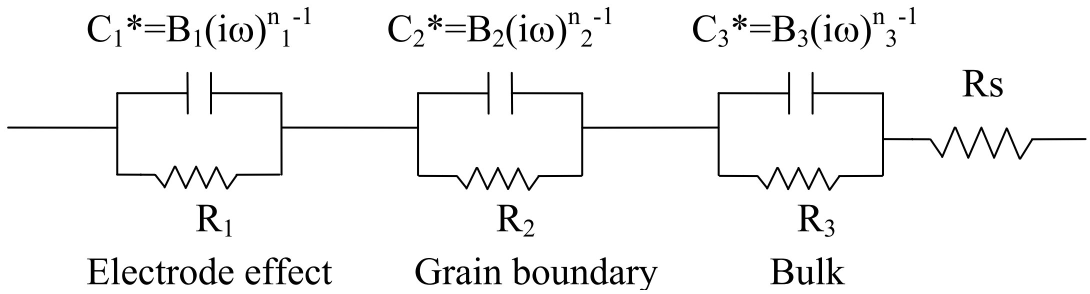

Figure 4: Equivalent circuit used to model the $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ response.

Table 1: List of fitting parameter for electrode effect, grain boundary and bulk for $Ca_{0.9}Sr_{0.1}Cu_3Ti_4O_{12}$ at 190 °C, 210 °C and 230 °C.

Temperature (°C)	**Universal capacitor**			**Resistance**	**Rs(Ω)**
Electrode Effect	**B_1(ΩHz)$^{-1}$**	**n_1**	**ω_p (Hz)**	**R_1 (Ω)**	
190 °C	2.294 e-6	0.72	22	21000	10
210 °C	1.369 e-6	0.65	40	12000	10
230 °C	1.011 e-6	0.68	50	5200	40
Grain Boundary	**B_2(ΩHz)$^{-1}$**	**n_2**	**ω_p (Hz)**	**R_2(Ω)**	**Rs(Ω)**
190 °C	2.763 e-9	0.89	1700	94000	10
210 °C	3.252 e-9	0.89	3500	42000	10
230 °C	4.270 e-9	0.88	6000	22000	40
Bulk	**B_3(ΩHz)$^{-1}$**	**n_3**	**ω_p (Hz)**	**R_3(Ω)**	**Rs(Ω)**
190 °C	1.811e-11	0.98	260000	4500	10
210 °C	2.657e-11	0.96	400000	2700	10
230 °C	1.675e-11	1.00	500000	1900	40

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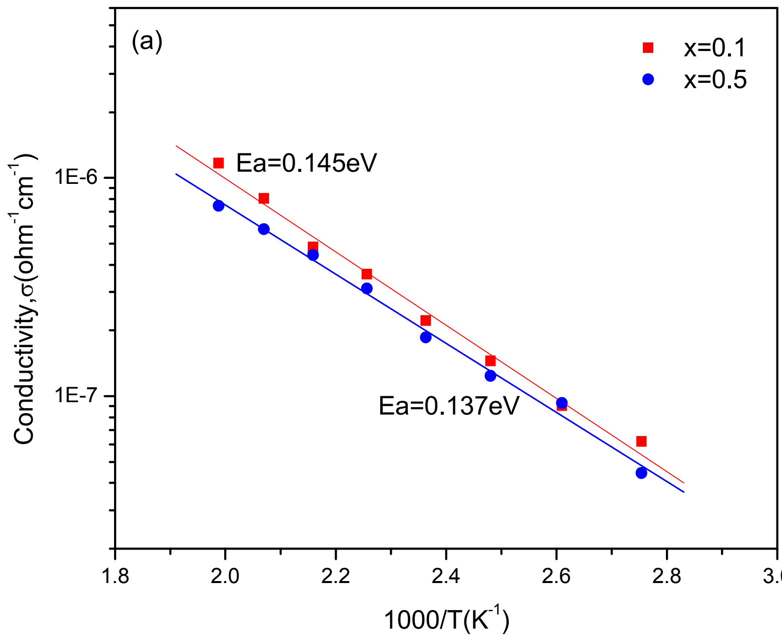

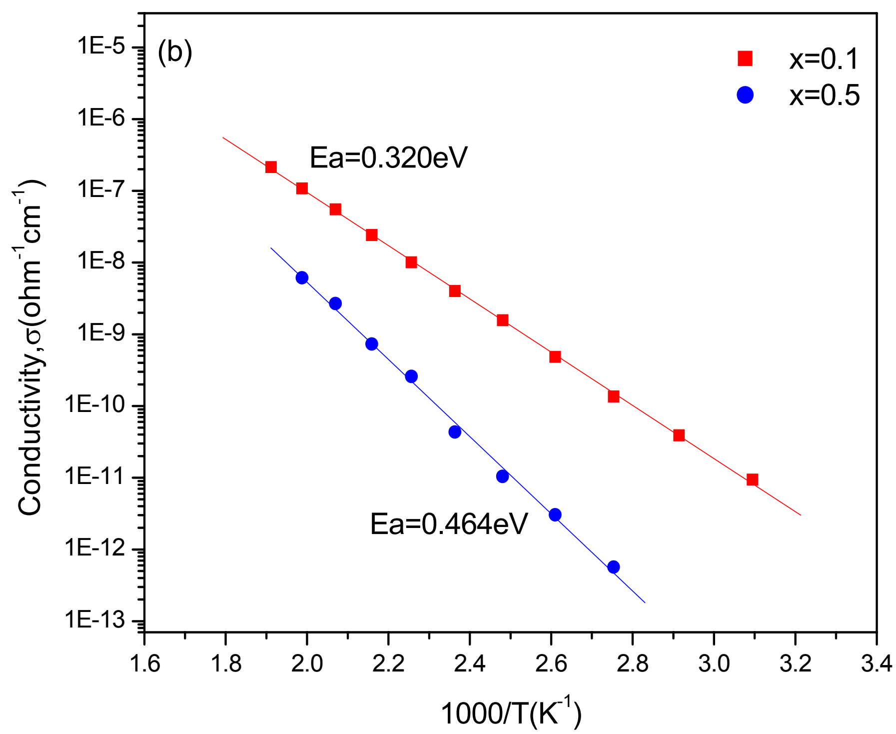

Figure 5: Arrhenius plot of (a) bulk conductivity and (b) grain boundary conductivity of $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ (x = 0.1 and 0.5) ceramics sintered at 1050 ^{o}C.

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CONCLUSION

The x-ray diffraction patterns for $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ with x = 0.0, 0.1 and 0.5 show single phase. Impedence response of polycrystalline samples shows three semicircular arcs and modeled by the series combination of three parallel RC circuits represent bulk, grain boundary and electrode effects response. The activation energy, E_a value for x = 0.1 are 0.145 eV and 0.320 eV for bulk and grain boundary regions, respectively. Meanwhile, the E_a value for x = 0.5 are 0.137 eV for the bulk regions, and 0.464 eV for grain boundary regions.

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