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UNIVERSITI PUTRA MALAYSIA

ELECTRICAL CHARACTERIZATION OF $Ca_{1-x}A_xCu_3Ti_4O_{12}$ (A = Sr OR Ba) WITH x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 CERAMICS.

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By

MAZNI BINTI MUSTAFA

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

Sept 2008

DEDICATION

This special dedication goes to my family especially my beloved mother Faridah Amin, in remembrance of Mustafa Lakim, my brother, sister, relatives and friends who have provided so much love, support, understanding and inspiration through the years.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science.

ELECTRICAL CHARACTERIZATION OF $Ca_{1-x}A_xCu_3Ti_4O_{12}$ (A = Sr OR Ba) WITH x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 CERAMICS.

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Sept 2008

Chairman: Associate Professor W. Mohamad Daud W. Yusoff, PhD

Faculty : Science

$CaCu_3Ti_4O_{12}$ (CCTO) has attracted an attention based on its extraordinary dielectric properties and makes it applicable to a microelectronic device application for capacitive element. Polycrystalline of CCTO, $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ (CSCTO) and $Ca_{1-x}Ba_xCu_3Ti_4O_{12}$ (CBCTO) with x = 0.1, 0.2, 0.3, 0.4 and 0.5 ceramics oxide were prepared using solid state reaction technique. The XRD patterns for all samples show the single phase peak and the calculated lattice parameter for CCTO is 'a' = 7.3870 Å. The SEM images show that the grain size was significantly increases with doping and consist of grain and grain boundary.

The value of dielectric permittivity of CCTO at 1 kHz increases with temperatures from 2740 at 70 ^oC to 3560 at 250 ^oC. The complex impedance plot shows three semicircle arcs indicating that the electrical processes in the

material due to the contribution from the grain at high frequencies, the grain boundary at intermediate frequencies and the electrode effect at low frequencies. The behaviour was modeled using equivalent RC circuit consisting of three parallel resistors, R and the universal capacitors, C^*. The grain resistance, R_g and the grain boundary resistance, R_{gb} decrease with temperatures.

The conductivity plots for all the samples show two clear regions due to the grain boundaries at low frequency and grain at high frequency. The value of n obtained by fitting the grain region at high frequency dependent decreases with temperatures with the value higher than 0.6 indicating that the conduction is due to hopping of electrons among Ti^{4+} and Ti^{3+}. A close similarity of the relaxation and conductivity activation energy values indicates that the processes may be attributed to the same type of charge carriers.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains.

SIFAT ELEKTRIK BAGI SERAMIK $Ca_{1-x}A_xCu_3Ti_4O_{12}$ (A = Sr ATAU Ba) DENGAN x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5.

Oleh

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Sept 2008

Pengerusi: Profesor Madya W. Mohamad Daud W. Yusoff, PhD

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$CaCu_3Ti_4O_{12}$ (CCTO) telah menarik perhatian berdasarkan sifat dielektrik yang luarbiasa dan membuatkan ia boleh digunakan pada aplikasi alat mikroelektronik bagi element kapasitif. Polikristal CCTO, $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ (CSCTO) dan $Ca_{1-x}Ba_xCu_3Ti_4O_{12}$ (CBCTO) dengan x 0.1, 0.2, 0.3, 0.4, dan 0.5 seramik oksida disediakan menggunakan teknik tindakbalas keadaan pepejal. Corak XRD bagi semua sampel menunjukkan satu puncak fasa dan nilai parameter kekisi bagi CCTO adalah 'a'= 7.3870 Å. Imej SEM menunjukkan saiz butiran meningkat dengan dop dan mengandungi butiran dan sempadan butiran.

Nilai ketelusan dielektrik bagi CCTO pada 1 kHz meningkat dengan suhu dari 2740 pada 70 ^{o}C ke 3560 pada 250 ^{o}C. Plot impedans kompleks menunjukkan tiga lengkungan separa bulatan yang menandakan proses elektrik di dalam

bahan terjadi akibat dari sumbangan butiran pada frekuensi tinggi, sempadan butiran pada frekensi pertengahan dan kesan elektrod pada frekuensi rendah. Sifat ini dimodel menggunakan litar setara RC mengandungi tiga litar selari mangandungi perintang, R dan kapasitor universal, C^*. Kerintangan butiran R_g dan kerintangan sempadan butiran R_{gb} meningkat dengan suhu.

Plot kekonduksian bagi semua sampel menunjukkan dengan jelas dua bahagian disebabkan dari sempadan butiran di frekuensi rendah dan butiran di frekuensi tinggi. Kawasan butiran pada frekuensi tinggi dimodel dan nilai n yang diperolehi menurun dengan suhu dan nilainya adalah lebih dari 0.6 menunjukkan konduksi adalah disebabkan oleh loncatan oleh elektron di antara Ti^{4+} dan Ti^{3+}. Persamaan pada nilai tenaga pengaktifan santaian dan kekonduksian menandakan bahawa proses adalah disebabkan oleh pembawa cas yang sama.

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I certify that an Examination Committee has met on 19th September 2008 to conduct the final examination of Mazni Bt. Mustafa on her Master Science thesis entitled "Electrical Characterization of $Ca_{1-x}A_xCu_3Ti_4O_{12}$ (A = Sr OR Ba) with x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 Ceramics" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisor Committee were as follows:

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Date: 30 December 2008

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously and is not concurrently submitted for any other degree at UPM or at any other institution.

MAZNI BT. MUSTAFA

Date: 19th September 2008

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LIST OF ABBREVIATION/NOTATION/GLOSSARY OF TERMS

ε^*	Complex permittivity
ε'	Dielectric permittivity
ε''	Dielectric
σ	Conductivity
$\sigma(\omega)$	Conductivity as a function of angular frequency
τ	Relaxation time(sec)
χ'	Real part of dielectric susceptibility
χ''	Imaginary part of dielectric susceptibility
ω	Angular frequency
Ω	Ohm
Å	Angstrom
eV	Electron volt
exp	Exponential
f	Frequency
i	$\sqrt{-1}$
k	Boltzmann constant
kHz	Kilohertz
ln	Natural logarithm
log	Logarithm
$\longrightarrow$	Goes to
$<$	Smaller than
$>$	Bigger than

~	Approximately
Ac	Alternating current
C^*	Complex capacitance
C'	Real part of capacitance
C"	Imaginary part of capacitance
DC	Direct current
E_a	Activation energy
G	Conductance
Hz	Hertz
Im	Imaginary part
K	Kelvin
M^*	Complex modulus
M'	Real part of modulus
M"	Imaginary part of modulus
R	Resistance
Re	Real part
UPM	Universiti Putra Malaysia
V	Voltage
XRD	X-ray diffraction
Y^*	Complex admittance
Y'	Real part of admittance
Y″	Imaginary part of admittance
Z^*	Complex impedance

Z’	Real part of impedance
Z”	Imaginary part of impedance

CHAPTER 1

RESEARCH OVERVIEW

1.1 Introduction

In recent years, colossal dielectric constant (CDC) materials exhibit high dielectric constant ε' value which greater than 1000 have attracted enormous of interests which lead to significant advances in the miniaturization of electronic applications. In the last few decades, microwave telecommunication and satellite broadcasting industries have progressed greatly through portable telephones and have benefited greatly from the miniaturization of various discrete components, especially the dielectric related components such capacitors, resonators, filters and thus reduces the size of the devices.

The CDC materials usually found in oxide ceramics and widely used since the ceramics processing are low in cost and reliable for electronic applications such capacitor. The volume efficiency of a capacitor is directly related to its dielectric constant and there have been an intensive researches on high dielectric constant materials since the higher the dielectric constant, the more charge can be stored and smaller devices will be produced.

In the former years the large dielectric response is a consequence of charge polarization due to ferroelectric displacement of the central ion in the unit cell. The barium titanate $BaTiO_3$, are well known ferroelectric material for more than 50 years because of its high dielectric constant value which is in the range of 2000 to 10000 at room temperature (Herbert *et al.*, 1993). $BaTiO_3$ have strong temperature dependence on ε' around the transition temperature and has a ferroelectric transition to a tetragonal structure accompanied by a rotation of the TiO_6 octahedra at 393 K. This structural transition is undesirable for many electronic device applications because it is often required that the dielectric permittivity of the material to be constant over as wide a temperature range as possible.

Recent scientific research and technical interest has attracted significant attention from the discovery of colossal dielectric constant in $CaCu_3Ti_4O_{12}$ (CCTO) ceramics. The discovery of a room temperature cubic perovskite compound CCTO sparked the interest in new materials that might not be limited by frequency and temperature. These uniqueness properties allow broadly application in microelectronic component and plays important role in creating high technology electronic devices.

CCTO was discovered in 1979 (Bochu *et al.*, 1979) and reported to have high dielectric constant exceeding 10,000 at 1 kHz (Subramanian *et al.*, 2002) and show good temperature stability from room temperature to 600 K. However, its dielectric constant drop rapidly to less than 100 below 100 K. CCTO also has no structural transition as a function of temperature and pressure in a cubic structure down to the lowest temperature. Numerous researches have been carried out to explore its properties and to probe the origin of the CDC. It is widely accepted that the CDC mechanism is extrinsic in origin due to the electrically heterogeneous microstructure in CCTO ceramics (Sinclair *et al.*, 2002).