



**UNIVERSITI PUTRA MALAYSIA**

**MICROSTRUCTURE AND GIANT DIELECTRIC PERMITTIVITY OF  
TITANO-MANGANITE SYSTEMS**

**WALTER CHARLES PRIMUS**

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**MICROSTRUCTURE AND GIANT DIELECTRIC PERMITTIVITY OF  
TITANO-MANGANITE SYSTEMS**

**By**

**WALTER CHARLES PRIMUS**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,  
in Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

**October 2008**



## **DEDICATION**

I dedicate this thesis to my family especially my beloved father and mother and also to all my friends.



Abstract of thesis presented to Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Doctor of Philosophy

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**October 2008**

**Chairman: Professor Abdul Halim Bin Shaari, PhD**

**Faculty: Science**

The microstructural and dielectric properties of  $\text{La}_{0.4}\text{Ba}_{0.6-x}\text{Ca}_x\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$  ( $x = 0.0, 0.2, 0.4, 0.6; 0.0 \leq y \leq 0.6$ ) ceramic systems have been investigated. The samples were prepared using solid-state technique where calcinations was done at 950 °C for 24 hours and sintered at 1300 °C for 3 hours after three times heating of 72 hours at 1300 °C.

Surface morphology study showed a well define grain and grain boundary and no changes in grain size when Ba ions substituted with Ca ions. However, the grains size becomes smaller from  $\sim 7 \mu\text{m}$  to  $\sim 1.5 \mu\text{m}$  as Sn ions were introduced into the Ti site of titano-manganite samples. At high Sn concentrations, the grain boundaries become smeared. The atomic percentage obtained from EDX analysis shows small deficits  $\pm 0.05$  with the calculated percentage. In XRD analysis, the  $\text{La}_{0.4}\text{Ba}_{0.6-x}\text{Ca}_x\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$  samples with  $x = 0.0$  and  $0.2$  are cubic structure ( $Pm-3m$ ) and distorted to a tetragonal structure ( $I4mcm$ ) as the composition of  $x = 0.4$  and  $0.6$ . Substituted Ti ions with Sn ions cause the samples structure change from tetragonal to orthorhombic ( $Pnma$ ).



A huge dielectric permittivity values  $> 100,000$  was obtained at lower frequency (10 Hz) and at higher temperatures (200 °C) for  $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$  and  $\text{La}_{0.4}\text{Ba}_{0.4}\text{Ca}_{0.2}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$  samples in dielectric measurement. At 1 kHz, the permittivity of  $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$  compound is  $\sim 20,000$  at 0 °C and slightly increases to  $\sim 54,000$  at 125 °C with low loss tangent  $\sim 0.8$ . While for  $\text{La}_{0.4}\text{Ba}_{0.4}\text{Ca}_{0.2}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$  compound, the permittivity at 1 kHz is  $\sim 56,000$  at 50 °C and increase to  $\sim 97,000$  at 100 °C with the loss tangent  $\sim 0.7$ . For  $\text{La}_{0.4}\text{Ba}_{0.2}\text{Ca}_{0.4}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$  and  $\text{La}_{0.4}\text{Ca}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$  samples, the values of dielectric permittivity are  $\sim 10,000$  over three order of frequency magnitude and also show thermal stability. However, the permittivity at 1 MHz is within 100 to 200 for all samples. The high permittivity values at low frequency are due to the grain boundary effect whereas the low permittivity values at high frequency are attributes from the bulk effect. Doping with Sn ions decreases the magnitude of grain boundary permittivity at low frequencies and increases the loss factor.

A Debye-like polarization behaviour with dc conduction are observed in the master plot. The relaxation peak and the dc conductivity in this titano-manganite compound were explained due to the trap-controlled hopping mechanism since the sample is dominated by electronic carriers. In traps phenomenon, delayed electronic transitions make a significant contribution to the complex dielectric permittivity. However, the decreases of the grain boundary magnitude at low frequency as the Sn ions increased resulting in the formation of anomalous low frequency dispersion (ALFD). In equivalent circuit modeling, the electrical property of the samples has been represented by a series combination of quasi-dc response, conductance and high frequency capacitance in parallel. The proposed model is in consistent with the

outcome in complex impedance analysis and surface morphology observation consisting grains and grain boundaries.

The conductivity of all samples obeys the empirical equations  $\sigma(\omega) = \sigma_{dc} + A\omega^n$ . Each of the bulk and grain boundary response gives the shape of the empirical equation. The dc conductivity of the grain and grain boundary are fall in the range of semiconducting materials ( $\sim 10^{-5}$  S/m to  $\sim 1$  S/m from -100 °C to 200 °C). The analysis of conductivity reveals that the sample is p-type semiconductors with holes as the majority carriers. The increase of Sn ions increased the grain boundary conductivity causing overlapping with the bulk conductivity. The grain boundary region is more thermally activated than the bulk region where the activation energy of the grain boundary is in the range of 0.31 to 0.54 eV and 0.17 to 0.37 eV for the bulk. The activation energy obtained is consistent with an electron hopping mechanism.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**MIKROSTRUKTUR DAN KETELUSAN DIELEKTRIK GERGASI BAGI  
SISTEM TITANO-MANGANITE**

Oleh

**WALTER CHARLES PRIMUS**

**Oktober 2008**

**Pengerusi: Professor Abdul Halim Bin Shaari, PhD**

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Kajian ke atas sistem seramik  $\text{La}_{0.4}\text{Ba}_{0.6-x}\text{Ca}_x\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$  ( $x = 0.0, 0.2, 0.4, 0.6$ ;  $0.0 \leq y \leq 0.6$ ) telah dilaksanakan bagi mengkaji mikrostruktur dan sifat dielektriknya. Penyediaan sampel menggunakan teknik keadaan pepejal dimana presinter dilakukan selama 24 jam pada suhu  $950\text{ }^\circ\text{C}$  dan disinter selama 3 jam pada suhu  $1300\text{ }^\circ\text{C}$  selepas tiga kali dipanaskan dalam tempoh 72 jam pada suhu  $1300\text{ }^\circ\text{C}$ .

Hasil cerapan terhadap permukaan mikrostruktur menunjukkan pembentukan butiran dan sempadan butiran sangat jelas dan tiada perubahan pada saiz butiran bila ion Ca menggantikan ion Ba. Walau bagaimanapun, saiz butiran tersebut menjadi semakin kecil daripada  $\sim 7\ \mu\text{m}$  ke  $\sim 1.5\ \mu\text{m}$  apabila ion Sn dimasukkan ke bahagian Ti bagi sampel titano-manganite. Pada konsentrasi Sn tinggi, sempadan butiran telah lebur. Jumlah peratusan atom yang diperolehi melalui EDX analisis menunjukkan sedikit kekurangan  $\pm 0.05$  dibandingkan dengan jumlah peratus pengiraan. Dalam analisis XRD, sampel  $\text{La}_{0.4}\text{Ba}_{0.6-x}\text{Ca}_x\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$  bagi  $x = 0.0$  dan  $0.2$  mempunyai struktur kubik ( $Pm-3m$ ) dan terherot ke struktur tetragonal ( $I4mcm$ ) pada komposisi  $x = 0.4$

dan 0.6. Penggantian ion Ti dengan ion Sn menyebabkan struktur sampel berubah daripada tetragonal ke orthohombik (*Pnma*).

Nilai ketelusan dielektrik yang besar  $> 100,000$  telah diperoleh pada frekuensi rendah (10 Hz) dan pada suhu tinggi (200 °C) bagi sampel  $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$  dan  $\text{La}_{0.4}\text{Ba}_{0.4}\text{Ca}_{0.2}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$  dalam pengukuran dielektrik. Pada 1 kHz, ketelusan bagi sebatian  $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$  ialah  $\sim 20,000$  pada 0 °C dan meningkat ke  $\sim 54,000$  pada 125 °C dengan kehilangan tangent  $\sim 0.8$  yang rendah. Manakala bagi sebatian  $\text{La}_{0.4}\text{Ba}_{0.4}\text{Ca}_{0.2}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ , ketelusan pada 1 kHz ialah  $\sim 56,000$  pada 50 °C dan meningkat ke  $\sim 97,000$  pada 100 °C dengan kehilangan tangen  $\sim 0.7$ . Bagi sample  $\text{La}_{0.4}\text{Ba}_{0.2}\text{Ca}_{0.4}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$  dan  $\text{La}_{0.4}\text{Ca}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6}\text{O}_3$ , nilai ketelusan dielektrik ialah  $\sim 10,000$  sehingga tiga tertib bagi jarak frekuensi dan menunjukkan kestabilan terma. Walau bagaimanapun, ketelusan pada 1 MHz ialah diantara 100 ke 200 bagi semua sampel. Nilai ketelusan yang tinggi pada frekuensi rendah adalah kesan sempadan butiran manakala nilai ketelusan yang rendah pada frekuensi tinggi adalah kesan sifat butiran. Penggantian dengan ion Sn telah merendahkan nilai ketelusan sempadan butiran di frekuensi rendah dan meningkatkan faktor kehilangan.

Sifat seperti pengutuban Debye berserta pengkonduksian arus terus boleh diperhatikan dalam plot penormalan. Puncak relaxsasi dan kekonduksian pada sebatian titano-manganis dijelaskan menggunakan mekanisma perangkap loncatan terkawal bagi sampel yang didominasi oleh pembawa elektronik. Dalam fenomena perangkap, penanguhan peralihan elektronik memberikan sumbangan ketara pada kompleks ketelusan dielektrik. Walau bagaimanapun, penurunan nilai sempadan butiran kepada  $\sim 100$  dengan peningkatan ion Sn, menyebabkan pembentukan



penyebaran frekuensi rendah yang luarbiasa (ALFD). Dalam model litar elektrik, sifat elektrik telah diwakilkan dengan gabungan sesiri bagi tindakbalas separa dc, konduktan dan kapasitan frekuensi tinggi secara selari. Model yang dicadangkan adalah konsisten dengan hasil analisis kompleks impedens dan cerapan morfologi permukaan yang terdiri daripada butiran dan sempadan butiran.

Kekonduksian bagi semua sampel mematuhi persamaan empirikal  $\sigma(\omega) = \sigma_{dc} + A\omega^n$ . Setiap satu tindakbalas bagi butiran dan sempadan butiran menghasilkan bentuk seperti persamaan empirikal. Kekonduksian bagi butiran dan sempadan butiran jatuh dalam lingkungan bahan semikonduktor ( $\sim 10^{-5}$  S/m ke  $\sim 1$  S/m daripada  $-100$  °C ke  $200$  °C). Analisis bagi jenis konduktiviti menunjukkan bahawa sampel tersebut adalah semikonduktor jenis-p dengan lohong sebagai pembawa meyoriti. Peningkatan ion Sn juga meningkatkan kekonduksian sempadan butiran menyebabkan pertindihan dengan kekonduksian butiran. Bahagian sempadan butiran lebih teraktif secara terma berbanding bahagian butiran di mana tenaga pengaktifan bagi sempadan butiran ialah dalam julat  $0.31$  hingga  $0.54$  eV dan  $0.17$  hingga  $0.37$  eV bagi butiran. Tenaga pengaktifan yang diperolehi adalah konsisten dengan mekanisme elektron loncatan.

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Finally, the most appreciation I would like to express is to my family, especially to my father, Charles Primus and my mother, Margaret Pang Sue Yin for their support, encouragement and prayer.



I certify that an examination committee met on 23<sup>rd</sup> October 2008 to conduct the final examination of Walter Charles Primus on his Doctor of Philosophy thesis entitled “Microstructure and Giant Dielectric Permittivity of Titano-Manganite Systems” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 1981. The Committee recommends that the candidate be awarded the degree of Doctor of Philosophy.

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Date: 15 January 2009



## **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 Universiti Putra Malaysia or at any other institution.

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**WALTER CHARLES PRIMUS**

Date: 26 December 2008

## TABLE OF CONTENTS

	<b>Page</b>
<b>DEDICATION</b>	ii
<b>ABSTRACT</b>	iii
<b>ABSTRAK</b>	vi
<b>ACKNOWLEDGEMENTS</b>	ix
<b>APPROVAL</b>	x
<b>DECLARATION</b>	xii
<b>LIST OF TABLES</b>	xv
<b>LIST OF FIGURES</b>	xvii
<b>LIST OF PLATE</b>	xxii
<b>LIST OF ABBREVIATIONS/NOTATIONS/GLOSSARY OF TERMS</b>	xxiii

### CHAPTER

<b>1</b>	<b>RESEARCH OVERVIEW</b>	<b>1</b>
	1.1 Introduction	1
	1.2 Brief Research overview	2
	1.3 Objective	3
<b>2</b>	<b>LITERATURE REVIEW</b>	<b>4</b>
	2.1 Dielectric Ceramic Systems	4
<b>3</b>	<b>THEORY</b>	<b>8</b>
	3.1 Crystal Structure	8
	3.2 Rietveld Analysis	9
	3.3 Dielectric Properties	11
	3.4 Dielectric Polarization and Relaxation Mechanisms	19
	3.5 Dielectric Phenomena in Semiconductor	24
	3.6 Fitting Response and Equivalent Circuit Modeling	31
	3.7 Immittance Formalisms	33
	3.8 Immittance Spectroscopy	34
	3.9 Alternating Current Conductivity	36
<b>4</b>	<b>METHODOLOGY</b>	<b>37</b>
	4.1 Sample Preparation	37
	4.2 Characterization Equipment	39
	4.2.1 X-Ray Diffraction (XRD)	39
	4.2.2 Scanning Electron Microscope (SEM)	40
	4.2.3 Energy Dispersive X-ray (EDX)	41
	4.2.4 Impedance Analyzer	41
	4.2.5 Conductivity Type Measurement	42
	4.3 Experiment Error	43



5	<b>RESULTS AND DISCUSSION</b>	44
	5.1 Surface Morphology	44
	5.2 Elemental Analysis	50
	5.3 Crystal Structure Analysis	52
	5.4 Frequency Dependence of Dielectric Properties	63
	5.5 Temperature Dependence of Dielectric Properties	75
	5.6 Master Plot of Complex Capacitance	92
	5.7 Complex Plane Analysis	105
	5.8 Electrical Circuit Modeling	119
	5.9 AC Conductivity	128
6	<b>CONCLUSIONS AND SUGGESTION</b>	135
	6.1 Conclusion	135
	6.2 Suggestions	137
	<b>REFERENCES</b>	139
	<b>APPENDICES</b>	144
	<b>BIODATA OF STUDENT</b>	149



## LIST OF TABLES

<b>Table</b>	<b>Page</b>
2.1.1 The summary of various spectral functions and their power law exponents	18
4.1.1 List of Chemicals	38
4.1.2 First series of $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples abbreviation	38
4.1.3 Second series of $\text{La}_{0.4}\text{Ba}_{0.4}\text{Ca}_{0.2}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples abbreviation	38
4.1.4 Third series of $\text{La}_{0.4}\text{Ba}_{0.2}\text{Ca}_{0.4}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples abbreviation	39
4.1.5 Forth series of $\text{La}_{0.4}\text{Ca}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples abbreviation	39
5.2.1 Elemental composition of $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples	50
5.2.2 Elemental composition of $\text{La}_{0.4}\text{Ba}_{0.4}\text{Ca}_{0.2}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples	51
5.2.3 Elemental composition of $\text{La}_{0.4}\text{Ba}_{0.2}\text{Ca}_{0.4}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples	51
5.2.4 Elemental composition of $\text{La}_{0.4}\text{Ca}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples	51
5.3.1 Crystallographic data of Rietveld refinement for LBMT X-ray diffraction pattern at room temperature	56
5.3.2 Crystallographic data of Rietveld refinement for LB'CMT X-ray diffraction pattern at room temperature	56
5.3.3 Crystallographic data of Rietveld refinement for LBC'MT X-ray diffraction pattern at room temperature	56
5.3.4 Crystallographic data of Rietveld refinement for LCMT X-ray diffraction pattern at room temperature	57
5.3.5 Structural of $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples	59
5.3.6 Structural of $\text{La}_{0.4}\text{Ba}_{0.4}\text{Ca}_{0.2}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples	60





5.3.7	Structural of $\text{La}_{0.4}\text{Ba}_{0.2}\text{Ca}_{0.4}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples	61
5.3.8	Structural of $\text{La}_{0.4}\text{Ca}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples	62
5.5.1	Dielectric permittivity $\epsilon'$ and loss tangent D at three fixed frequencies for LBMT sample	88
5.5.2	Dielectric permittivity $\epsilon'$ and loss tangent D at three fixed frequencies for LBMTS3 sample	88
5.5.3	Dielectric permittivity $\epsilon'$ and loss tangent D at three fixed frequencies for LBMS sample	89
5.5.4	Dielectric permittivity $\epsilon'$ and loss tangent D at three fixed frequencies for LB'CMT sample	89
5.5.5	Dielectric permittivity, $\epsilon'$ and loss tangent D at three fixed frequencies for LB'CMTS4 sample	90
5.5.6	Dielectric permittivity $\epsilon'$ and loss tangent D at three fixed frequencies for LB'CMS sample	90
5.5.7	Dielectric permittivity $\epsilon'$ and loss tangent D at three fixed frequencies for LBC'MS sample	91
5.5.8	Dielectric permittivity $\epsilon'$ and loss tangent D at three fixed frequencies for LCMT sample	91
5.7.1	Fitting parameter of Figure 5.8.1 to 5.8.8 based on the electrical circuit in Figure 5.8.9, corresponding to the bulk and grain boundary effects	118

## LIST OF FIGURES

Figure		Page
2.1.1	Structure of ordered perovskite BaTiO <sub>3</sub>	5
3.4.1	The various types of interaction between the electromagnetic field and matter and the relevant relative permittivity	19
3.4.2	The polarization process with no electric field and with applied electric field	21
3.5.1	Four electrons in the manganese ion at the same spin state	25
3.5.2	The band diagram of a semiconductor	26
3.6.1	Bound dipolar response with electrical circuit modeling	32
3.6.2	Quasi free charge response with electrical circuit modeling	32
3.8.1	Three parallel circuit in series	34
3.8.2	The simulated (a) complex impedance and (b) modulus plots corresponding to two parallel circuits in series	35
4.2.1	Setup for determining conductivity type using rectification method	43
5.3.1	X-ray reflections for La <sub>0.4</sub> Ba <sub>0.6-x</sub> Ca <sub>x</sub> Mn <sub>0.4</sub> Ti <sub>0.6</sub> O <sub>3</sub> (x = 0.0, 0.2, 0.4 and 0.6) samples	54
5.3.2	Rietveld pattern of x-ray powder diffraction data for LBMT sample at room temperature	55
5.3.3	Rietveld pattern of x-ray powder diffraction data for LBC'MT sample at room temperature	55
5.3.4	Ball and stick structural model of (a) cubic structure of LBMT and (b) tetragonal structure of LBC'MT samples	57
5.3.5	X-ray reflections for La <sub>0.4</sub> Ba <sub>0.6</sub> Mn <sub>0.4</sub> Ti <sub>0.6-y</sub> Sn <sub>y</sub> O <sub>3</sub> (0.0 ≤ y ≤ 0.6) samples	59
5.3.6	X-ray reflections for La <sub>0.4</sub> Ba <sub>0.4</sub> Ca <sub>0.2</sub> Mn <sub>0.4</sub> Ti <sub>0.6-y</sub> Sn <sub>y</sub> O <sub>3</sub> (0.0 ≤ y ≤ 0.6) samples	60
5.3.7	X-ray reflections for La <sub>0.4</sub> Ba <sub>0.2</sub> Ca <sub>0.4</sub> Mn <sub>0.4</sub> Ti <sub>0.6-y</sub> Sn <sub>y</sub> O <sub>3</sub> (0.0 ≤ y ≤ 0.6) samples	61

5.3.8	X-ray reflections for $\text{La}_{0.4}\text{Ca}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples	62
5.4.1	Frequency dependence of the (a) dielectric permittivity $\epsilon'$ , (b) dielectric loss $\epsilon''$ and (c) loss tangent D of LBMT sample in the range of -100 to 200 °C	67
5.4.2	Frequency dependence of the (a) dielectric permittivity $\epsilon'$ , (b) dielectric loss $\epsilon''$ and (c) loss tangent D of LBMTS3 sample in the range of -100 to 150 °C	68
5.4.3	Frequency dependence of the (a) dielectric permittivity $\epsilon'$ , (b) dielectric loss $\epsilon''$ and (c) loss tangent D of LBMS sample in the range of -100 to 200 °C	69
5.4.4	Frequency dependence of the (a) dielectric permittivity $\epsilon'$ , (b) dielectric loss $\epsilon''$ and (c) loss tangent D of LB'CMT sample in the range of -100 to 200 °C	70
5.4.5	Frequency dependence of the (a) dielectric permittivity $\epsilon'$ , (b) dielectric loss $\epsilon''$ and (c) loss tangent D of LB'CMTS4 sample in the range of -100 to 150 °C	68
5.4.6	Frequency dependence of the (a) dielectric permittivity $\epsilon'$ , (b) dielectric loss $\epsilon''$ and (c) loss tangent D of LB'CMS sample in the range of -150 to 200 °C	72
5.4.7	Frequency dependence of the (a) dielectric permittivity $\epsilon'$ , (b) dielectric loss $\epsilon''$ and (c) loss tangent D of LBC'MTS6 sample in the range of -150 to 100 °C	73
5.4.7	Frequency dependence of the (a) dielectric permittivity $\epsilon'$ , (b) dielectric loss $\epsilon''$ and (c) loss tangent D of LCMT sample in the range of -150 to 125 °C	74
5.5.1	Dielectric permittivity $\epsilon'$ and loss tangent D versus temperatures at three fixed frequencies (a) 10 Hz, (b) 1 kHz and (c) 1 MHz for LBMT sample	80
5.5.2	Dielectric permittivity $\epsilon'$ and loss tangent D versus temperatures at three fixed frequencies (a) 10 Hz, (b) 1 kHz and (c) 1 MHz for LBMTS3 sample	81
5.5.3	Dielectric permittivity $\epsilon'$ and loss tangent D versus temperatures at three fixed frequencies (a) 10 Hz, (b) 1 kHz and (c) 1 MHz for LBMS sample	82

5.5.4	Dielectric permittivity $\epsilon'$ and loss tangent D versus temperatures at three fixed frequencies (a) 10 Hz, (b) 1 kHz and (c) 1 MHz for LB'CMT sample	83
5.5.5	Dielectric permittivity $\epsilon'$ and loss tangent D versus temperatures at three fixed frequencies (a) 10 Hz, (b) 1 kHz and (c) 1 MHz for LB'CMTS4 sample	84
5.5.6	Dielectric permittivity $\epsilon'$ and loss tangent D versus temperatures at three fixed frequencies (a) 10 Hz, (b) 1 kHz and (c) 1 MHz for LB'CMS sample	85
5.5.7	Dielectric permittivity $\epsilon'$ and loss tangent D versus temperatures at three fixed frequencies (a) 10 Hz, (b) 1 kHz and (c) 1 MHz for LBC'MS sample	86
5.5.8	Dielectric permittivity $\epsilon'$ and loss tangent D versus temperatures at three fixed frequencies (a) 10 Hz, (b) 1 kHz and (c) 1 MHz for LCMT sample	87
5.6.1	Normalized plots of the complex capacitance of LBMT sample against frequency from (a) -100 to 75 °C and (b) 25 to 200 °C.	97
5.6.2	Normalized plots of the complex capacitance of LBMTS3 sample against frequency from (a) -100 to 0 °C and (b) 25 to 200 °C	98
5.6.3	Normalized plots of the complex capacitance of LBMS sample against frequency from (a) -25 to 75 °C and (b) 75 to 200 °C	99
5.6.4	Normalized plots of the complex capacitance of LB'CMT sample against frequency from (a) -50 to 50 °C and (b) 50 to 200 °C	100
5.6.5	Normalized plots of the complex capacitance of LB'CMTS1 sample against frequency from (a) -100 to 25 °C and (b) 50 to 175 °C	101
5.6.6	Normalized plots of the complex capacitance of LB'CMTS5 sample against frequency from (a) -125 to 25 °C and (b) 50 to 175 °C	102
5.6.7	Normalized plots of the complex capacitance of LBC'MTS4 sample against frequency from (a) -125 to -50 °C and (b) -25 to 150 °C	103
5.6.8	Normalized plots of the complex capacitance of LCMTS1 sample against frequency from (a) -150 to -75 °C and (b) 50 to 75 °C	104



5.7.1	Complex plane of impedance $Z^*$ and modulus $M^*$ fitted with fitting response for LBMT sample at 0 °C, 50 °C and 100 °C	109
5.7.2	Complex plane of impedance $Z^*$ and modulus $M^*$ fitted with fitting response for LBMTS3 sample at -25 °C, 50 °C and 100 °C	110
5.7.3	Complex plane of impedance $Z^*$ and modulus $M^*$ fitted with fitting response for LBMS sample at -25 °C, 75 °C and 150 °C	111
5.7.4	Complex plane of impedance $Z^*$ and modulus $M^*$ fitted with fitting response for LB'CMT sample at 0 °C, 50 °C and 125 °C	112
5.7.5	Complex plane of impedance $Z^*$ and modulus $M^*$ fitted with fitting response for LB'CMTS4 sample at -25 °C, 50 °C and 125 °C	113
5.7.6	Complex plane of impedance $Z^*$ and modulus $M^*$ for LB'CMS sample at -50 °C, 25 °C and 100 °C	114
5.7.7	Complex plane of impedance $Z^*$ and modulus $M^*$ fitted with fitting response for LBC'MTS4 sample at -75 °C, 0 °C and 50 °C	115
5.7.8	Complex plane of impedance $Z^*$ and modulus $M^*$ fitted with fitting response for LCMTS5 sample at -100 °C, -50 °C and 25 °C	116
5.7.9	Circuit modeling represented the electrical behaviour of the samples in the impedance and modulus plane plots at selected temperatures	117
5.8.1	The normalization data of the real and imaginary part of LBMT sample fitted with fitting response	123
5.8.2	The normalization data of the real and imaginary part of LBMTS4 sample fitted with fitting response	123
5.8.3	The normalization data of the real and imaginary part of LBMTS5 sample fitted with fitting response	124
5.8.4	The normalization data of the real and imaginary part of LBMTS6 sample fitted with fitting response	124
5.8.5	The normalization data of the real and imaginary part of LB'CMT sample fitted with fitting response	125
5.8.6	The normalization data of the real and imaginary part of LB'CMTS6 sample fitted with fitting response	125

5.8.7	The normalization data of the real and imaginary part of LBC'MTS1 sample fitted with fitting response	126
5.8.8	The normalization data of the real and imaginary part of LBC'MTS5 sample fitted with fitting response	126
5.8.9	The normalization data of the real and imaginary part of LCMTS3 sample fitted with fitting response	127
5.8.10	The normalization data of the real and imaginary part of LCMTS5 sample fitted with fitting response	127
5.9.1	Double log plot of ac conductivity at various temperatures with Arrhenius plot for LBMT samples	131
5.9.2	Double log plot of ac conductivity at various temperatures with Arrhenius plot for LBMTS1 samples	131
5.9.3	Double log plot of ac conductivity at various temperatures with Arrhenius plot for LBMS samples	132
5.9.4	Double log plot of ac conductivity at various temperatures with Arrhenius plot for LB'CMT samples	132
5.9.5	Double log plot of ac conductivity at various temperatures with Arrhenius plot for LB'CMTS1 samples	133
5.9.6	Double log plot of ac conductivity at various temperatures with Arrhenius plot for LB'CMTS6 samples	133
5.9.7	Double log plot of ac conductivity at various temperatures with Arrhenius plot for LBC'MTS2 samples	134
5.9.8	Double log plot of ac conductivity at various temperatures with Arrhenius plot for LCMTS4 samples	134



## LIST OF PLATES

<b>Plate</b>		<b>Page</b>
5.1.1	SEM micrograph of $\text{La}_{0.4}\text{Ba}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples	46
5.1.2	SEM micrograph of $\text{La}_{0.4}\text{Ba}_{0.4}\text{Ca}_{0.2}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples	47
5.1.3	SEM micrograph of $\text{La}_{0.4}\text{Ba}_{0.2}\text{Ca}_{0.4}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples	48
5.1.4	SEM micrograph of $\text{La}_{0.4}\text{Ca}_{0.6}\text{Mn}_{0.4}\text{Ti}_{0.6-y}\text{Sn}_y\text{O}_3$ ( $0.0 \leq y \leq 0.6$ ) samples	49

## LIST OF SYMBOLS AND ABBREVIATIONS

$\delta$	Differentiation
$\varepsilon'$	Dielectric permittivity
$\varepsilon_{\text{inf}}$	Dielectric permittivity at very high frequency
$\varepsilon_r$	Relative dielectric permittivity
$\varepsilon(\omega)$	Dielectric permittivity as a function of angular frequency
$\theta$	Diffraction angle
$\lambda$	Wavelength
$\mu$	Micron
$\pi$	$= 180^\circ$
$\sigma$	Conductivity (mho/m)
$\sigma(\omega)$	Conductivity as a function of angular frequency
$\tau$	Relaxation time (sec)
$\chi'$	Real part of dielectric susceptibility
$\chi''$	Imaginary part of dielectric susceptibility
$\omega$	Angular frequency
$\omega_c$	Critical angular frequency
$\omega_p$	Peak angular frequency
$\Omega$	Ohm
$\text{\AA}$	Angstrom unit
eV	Electron volt
exp	Exponential
$f$	Frequency
fF	Femtofarad





$i$	$= \sqrt{-1}$
$k$	Boltzmann constant = $0.862 \times 10^{-4} \text{ eVK}^{-1}$
kHz	Kilohertz
ln	Natural logarithm
Log	Logarithm
GHz	GigaHertz
mHz	Milihertz
MHz	Megahertz
nF	Nanofarad
pF	Picofarad
$\propto$	Proportional to
$\rightarrow$	Goes to
$<$	Smaller than
$>$	Bigger than
$\sim$	Approximately
Ac	Alternating current
$B$	Susceptance (mho)
$C^*$	Complex Capacitance
$C'$	Real part of capacitance
$C''$	Imaginary part of capacitance
Dc	Direct current
$E_a$	Activation energy
EDX	Electron Dispersion X-ray
$G$	Conductance
Hz	Hertz