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UNIVERSITI PUTRA MALAYSIA

MICROSTRUCTURE AND GIANT DIELECTRIC PERMITTIVITY OF TITANO-MANGANITE SYSTEMS

WALTER CHARLES PRIMUS

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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

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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

MICROSTRUCTURE AND GIANT DIELECTRIC PERMITTIVITY OF TITANO-MANGANITE SYSTEMS

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October 2008

Chairman: Professor Abdul Halim Bin Shaari, PhD

Faculty: Science

The microstructural and dielectric properties of $La_{0.4}Ba_{0.6-x}Ca_xMn_{0.4}Ti_{0.6-y}Sn_yO_3$ (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 ~ 7 μm to ~ 1.5 μm 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 ± 0.05 with the calculated percentage. In XRD analysis, the $La_{0.4}Ba_{0.6-x}Ca_xMn_{0.4}Ti_{0.6}O_3$ samples with x = 0.0 and 0.2 are cubic structure (*Pm*-3*m*) and distorted to a tetragonal structure (*I*4*mcm*) 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 ºC) for $La_{0.4}Ba_{0.6}Mn_{0.4}Ti_{0.6}O_3$ and $La_{0.4}Ba_{0.4}Ca_{0.2}Mn_{0.4}Ti_{0.6}O_3$ samples in dielectric measurement. At 1 kHz, the permittivity of $La_{0.4}Ba_{0.6}Mn_{0.4}Ti_{0.6}O_3$ compound is ~ 20,000 at 0 ºC and slightly increases to ~ 54,000 at 125 ºC with low loss tangent ~ 0.8. While for $La_{0.4}Ba_{0.4}Ca_{0.2}Mn_{0.4}Ti_{0.6}O_3$ compound, the permittivity at 1 kHz is ~ 56,000 at 50 ºC and increase to ~ 97,000 at 100 ºC with the loss tangent ~ 0.7. For $La_{0.4}Ba_{0.2}Ca_{0.4}Mn_{0.4}Ti_{0.6}O_3$ and $La_{0.4}Ca_{0.6}Mn_{0.4}Ti_{0.6}O_3$ samples, the values of dielectric permittivity are ~ 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 (~ 10^{-5} S/m to ~ 1 S/m from -100 ºC to 200 ºC). 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

Fakulti: Sains

Kajian ke atas sistem seramik $La_{0.4}Ba_{0.6-x}Ca_xMn_{0.4}Ti_{0.6-y}Sn_yO_3$ (x = 0.0, 0.2, 0.4, 0.6; $0.0 \leq y \leq 0.6$) telah dilakukankan bagi mengkaji mikrostruktur dan sifat dielektriknya. Penyediaan sampel menggunakan teknik keadaan pepejal dimana presinter dilakukankan selama 24 jam pada suhu 950 °C dan disinter selama 3 jam pada suhu 1300 °C selepas tiga kali dipanaskan dalam tempoh 72 jam pada suhu 1300 °C.

Hasil cerapan terhadap permukaan mikrostruktur menunjukan pembentukan butiran dan sempadan butiran sangat jelas dan tiada perubahan pada saiz butiran bila ion Ca mengantikan ion Ba. Walau bagaimanapun, saiz butiran tersebut menjadi semakin kecil daripada ~ 7 μm ke ~ 1.5 μm apabila ion Sn dimasukan kebahagian Ti bagi sampel titano-manganite. Pada konsentrasi Sn tinggi, sempadan butiran telah lebur. Jumlah peratusan atom yang diperolehi melalui EDX analisis menunjukan sedikit kekurangan ± 0.05 dibandingkan dengan jumlah peratus pengiraan. Dalam analisis XRD, sampel $La_{0.4}Ba_{0.6-x}Ca_xMn_{0.4}Ti_{0.6}O_3$ bagi x = 0.0 dan 0.2 mempunyai struktur kubik (*Pm*-3*m*) dan terherot ke struktur tetragonal (*I*4*mcm*) pada komposisi x = 0.4

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

Nilai ketelusan dielektrik yang besar > 100,000 telah diperolehi pada frekuensi rendah (10 Hz) dan pada suhu tinggi (200 ºC) bagi sampel $La_{0.4}Ba_{0.6}Mn_{0.4}Ti_{0.6}O_3$ dan $La_{0.4}Ba_{0.4}Ca_{0.2}Mn_{0.4}Ti_{0.6}O_3$ dalam pengukuran dielektrik. Pada 1 kHz, ketelusan bagi sebatian $La_{0.4}Ba_{0.6}Mn_{0.4}Ti_{0.6}O_3$ ialah ~ 20,000 pada 0 ºC dan meningkat ke ~ 54,000 pada 125 ºC dengan kehilangan tangent ~ 0.8 yang rendah. Manakala bagi sebatian $La_{0.4}Ba_{0.4}Ca_{0.2}Mn_{0.4}Ti_{0.6}O_3$, ketelusan pada 1 kHz ialah ~ 56,000 pada 50 ºC dan meningkat ke ~ 97,000 pada 100 ºC dengan kehilangan tangen ~ 0.7. Bagi sample $La_{0.4}Ba_{0.2}Ca_{0.4}Mn_{0.4}Ti_{0.6}O_3$ dan $La_{0.4}Ca_{0.6}Mn_{0.4}Ti_{0.6}O_3$, nilai ketelusan dielektrik ialah ~ 10,000 sehingga tiga tertib bagi jarak frekuensi dan menunjukan 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 meggunakan mekanisma perangkap loncatan terkawal bagi sampel yang didominasi oleh pembawa elektronik. Dalam fenomena perangkap, penangguhan peralihan elektronik memberikan sumbangan ketara pada komplex ketelusan dielektrik. Walau bagaimanapun, penurunan nilai sempadan butiran kepada ~ 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 komplek 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 emperikal. Kekonduksian bagi butiran dan sempadan butiran jatuh dalam lingkungan bahan semikonduktor (~ 10^{-5} S/m ke ~ 1 S/m daripada -100 ºC ke 200 ºC). Analysis bagi jenis konduktiviti menunjukan bahawa sempel tersebut adalah semikonduktor jenis-p dengan lohong sebagai pembawa mejoriti. 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 mechanisma 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 23rd 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.

Members of the Examination Committee are as follows:

Elias Saion, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Kaida Khalid, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Jumiah Hassan, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Ibrahim Abu Talib, PhD
Professor
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
Malaysia
(External Examiner)

HASANAH MOHD. GHAZALI, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

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

ABDUL HALIM SHAARI, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

WAN MOHD. DAUD WAN YUSOFF, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

ZAINAL ABIDIN TALIB, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

HASANAH MOHD. GHAZALI, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

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.

WALTER CHARLES PRIMUS

Date: 26 December 2008

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δ	Differentiation
ε'	Dielectric permittivity
ε_{inf}	Dielectric permittivity at very high frequency
ε_r	Relative dielectric permittivity
$\varepsilon(\omega)$	Dielectric permittivity as a function of angular frequency
θ	Diffraction angle
λ	Wavelength
μ	Micron
π	= 180º
σ	Conductivity (mho/m)
$\sigma(\omega)$	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_c	Critical angular frequency
ω_p	Peak angular frequency
Ω	Ohm
Å	Angstrom unit
eV	Electron volt
exp	Exponential
f	Frequency
fF	Femtofarad

i	$= \sqrt{-1}$
k	Boltzmann constant = 0.862×10^{-4} eVK^{-1}
kHz	Kilohertz
In	Natural logarithm
Log	Logarithm
GHz	GigaHertz
mHz	Milihertz
MHz	Megahertz
nF	Nanofarad
pF	Picofarad
$\propto$	Proportional to
$\rightarrow$	Goes to
<	Smaller than
>	Bigger than
~	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