UNIVERSITI PUTRA MALAYSIA

THERMAL DIFFUSIVITY AND DIELECTRIC PROPERTIES OF STRONTIUM- DOPED BARIUM TITANATE AND CALSIUM TITANATE SYSTEMS.

NOOR JAWAD RIDHA

FS 2009 12

THERMAL DIFFUSIVITY AND DIELECTRIC PROPERTIES OF STRONTIUM- DOPED BARIUM TITANATE AND CALSIUM TITANATE SYSTEMS.

NOOR JAWAD RIDHA

MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA

2009

THERMAL DIFFUSIVITY AND DIELECTRIC PROPERTIES OF STRONTIUM- DOPED BARIUM TITANATE AND CALSIUM TITANATE SYSTEMS

By

NOOR JAWAD RIDHA

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

April 2009

DEDICATION

To my father soul

To my dearest mother

for her supports and prayer……

To my husband Firas Kamel Mohamad

who loves and support me all the times...

To my supervisors

Prof. Dr. W. Mahmood Mat Yunus,

Prof. Dr. Abdul Halim Shaari and Assoc. Prof. Dr. Zainal Abidin Talib

for their time and advice

To all my friends

for their assistance and supports…

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

THERMAL DIFFUSIVITY AND DIELECTRIC PROPERTIES OF STRONTIUM- DOPED BARIUM TITANATE AND CALSIUM TITANATE SYSTEMS

By

NOOR JAWAD RIDHA

April 2009

Chairman: W. Mahmood Mat Yunus, PhD

Faculty: Science

In this thesis, the structure, thermal diffusivity and dielectric constant of $Ba_{1-x}Sr_xTiO_3$ and $Ca_{1-x}Sr_xTiO_3$ ($0 \leq x \leq 1$) ceramics were investigated. The samples were prepared using solid-state reaction technique with a sintering temperature at 1200 °C. From XRD analysis, the $BaTiO_3$ structure obtained was tetragonal and then transformed to cubic; whilst, $CaTiO_3$ structure changed from orthorhombic to cubic with an intermediate tetragonal phase as the amount of Sr ions increased. Surface morphology studies showed that the grain size decreased with increasing Sr ions in both $Ba_{1-x}Sr_xTiO_3$ and $Ca_{1-x}Sr_xTiO_3$ systems.

Photoflash technique was used to determine the thermal diffusivity of $BaTiO_3$, $CaTiO_3$ and $SrTiO_3$ at room temperature. The effect of substitution Sr ions on the thermal diffusivity of $Ba_{1-x}Sr_xTiO_3$ and $Ca_{1-x}Sr_xTiO_3$ was also investigated. It was found that increasing Sr ions in $Ba_{1-x}Sr_xTiO_3$ samples reduced the thermal diffusivity value from 11.302×10^{-3} cm^2/s to 6.467×10^{-3} cm^2/s and accompanying by a decrease in density. Similarly, the thermal diffusivity values of $Ca_{1-x}Sr_xTiO_3$ system decreased from 13.11×10^{-3} cm^2/s to 6.467×10^{-3} cm^2/s as its density increased.

For thermal diffusivity measurement at higher temperature, laser flash technique was used. It was noticed that the thermal diffusivity of $Ba_{1-x}Sr_xTiO_3$ and $Ca_{1-x}Sr_xTiO_3$ decreased with increasing temperature from room temperature to 150 °C.

The dielectric properties of $BaTiO_3$, $CaTiO_3$ and $SrTiO_3$ were investigated at various temperatures from 25 to 150 °C using AC impedance analyzer. Increasing Sr ions in $BaTiO_3$ reduced the dielectric constant from 709 to 246 at frequency 10^6 Hz at room temperature. On the other hand, increasing Sr ions in $CaTiO_3$ raised the dielectric constant from 106 to 246, and the highest value was found at x = 0.2. The dielectric constant of $Ba_{1-x}Sr_xTiO_3$ decreased with increasing temperature. The highest dielectric constant value was recorded for $Ba_{1-x}Sr_xTiO_3$ system where x = 0 and 0.1 at phase change temperatures, 125 °C and 100 °C respectively.

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

RESAPAN TERMA DAN SIFAT DIELEKTRIK BARIUM TITANATE DAN KALASIAM TITANATE DIDOP DENGAN STRONTIUM

Oleh

NOOR JAWAD RIDHA

April 2009

Pengerusi: W. Mahmood Mat Yunus, PhD

Fakulti: Sains

Dalam tesis ini, struktur, resapan terma dan pemalar dielektrik bagi seramik $Ba_{1-x}Sr_xTiO_3$ dan $Ca_{1-x}Sr_xTiO_3$ ($0 \leq x \leq 1$) telah dikaji. Sampel telah disediakan dengan menggunakan teknik tindak balas pepejal dan disinter pada suhu 1200 °C. Daripada analisis XRD, struktur $BaTiO_3$ didapati berubah dari tetragonal kepada struktur kubus, manakala bagi struktur $CaTiO_3$, didapati berubah dari ortorombik kepada struktur kubus dengan pertengahan fasa tetragonal apabila ion Sr bertambah. Kajian morfologi permukaan menunjukkan bahwa saiz butiran mengecil dengan meningkatnya Sr ions di dalam kedua- dua sistem $Ba_{1-x}Sr_xTiO_3$ dan $Ca_{1-x}Sr_xTiO_3$.

Teknik fotokilat telah digunakan untuk menentukan resapan terma $BaTiO_3$, $CaTiO_3$ dan $SrTiO_3$ pada suhu bilik. Kesan penggantian ion Sr terhadap respon terma dalam $BaTiO_3$ dan $CaTiO_3$ juga telah dikaji. Didepeti bahawa pertambahan ion Sr di dalam sampel $BaTiO_3$ mengurangkan nilai kadar resapan terma dari 11.302×10^{-3} cm^2/s kepada 9 6.467×10^{-3} cm^2/s, dan diikuti dengan penurunan dalam ketumpatan.

Serupa juga, nilai resapan terma sistem $Ca_{1-x}Sr_xTiO_3$ berkurangan dari 13.11×10^{-3} cm^2/s kepada 6.467×10^{-3} cm^2/s, sebaliknya nilai ketumpatan bertambah.

Untuk pengukuran resapan terma pada suhu yang lebih tinggi, teknik kilatan laser telah digunakan. Didapati bahawa resapan terma bagi $Ba_{1-x}Sr_xTiO_3$ dan $Ca_{1-x}Sr_xTiO_3$ menurun dengan kenaikan suhu dari 25 °C hingga 150 °C.

Sifat dielektrik $BaTiO_3$, $CaTiO_3$ dan $SrTiO_3$ diukur pada belbagai suhu dalam julat 25 °C hingga 150 °C dengan menggunakan penganalisis impedans. Pertambahan ion Sr dalam $BaTiO_3$ telah mengurangkan pemalar dielektrik (pada 10^6 Hz) dari 709 kepada 246. Sementara itu, pertambahan ion Sr dalam $CaTiO_3$ meningkatkan pemalar dielektrik dari 106 kepada 246, dan nilai tertinggi dicapai pada $x = 0.2$. disamping itu, pemalar dielektrik bagi sistem $Ba_{1-x}Sr_xTiO_3$ dengan $x= 0$ dan 0.1 didapati pada suhu perubahan fasa 100 °C dan 125 °C.

ACKNOWLEDGEMENTS

First, I am very grateful to Allah s.w.t. for giving me the strength and patience to produce this thesis.

I would like to express my highest respect and utmost gratitude to my supervisor, Prof. Wan Mahmood Mat Yunus, and to my co-supervisors, Prof. Dr. Abdul Halim Shaari and Assoc. Prof. Dr. Zainal Abidin Talib who have been giving me advices and guidance throughout the whole project.

Special thanks to Assoc. Prof. Dr. Wan Mohd. Daud Wan Yusoff for his explanations and guidance which provided me with scientific knowledge.

My deepest gratitude to my family, especially to my husband, my mother, my brothers and sisters, my mother-in-law and my father-in-law for their material and spiritual support, encouragement, prayer and the immeasurable love given to me keeping me living in comfortable and peaceful conditions. My special thanks to my son Ahmad for his love and time he missed his mother.

My thanks will not be complete until I acknowledge my friends Walter, Josephine, Thai and Azizah for great supports and help during whole study.

My thanks also go to all faculty members of the Physics Department especially to XRD staff and material lab staff for their help during this study.

I certify that an Examination Committee has met on 28 April 2009 to conduct the final examination of Noor Jawad Ridha on her Master of Science thesis entitled "Thermal Diffusivity and Dielectric Constant of Strontium- Doped Barium Titanate and Calcium Titanate Systems" in accordance with Universiti Putra Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the degree of Master of Science.

Members of the Examination Committee were as follows:

Kaida Bin Khalid, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mohd. Maarof H. A. Maksin, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Tan Kar Ban, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Mohamad Deraman, PhD
Professor
Faculty of Science
Universiti Kebangsaan Malaysia
(External Examiner)

Bujang Kim Huat, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 29 May 2009

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

W. Mahmood Mat Yunus, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Abdul Halim Shaari, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Zainal Abidin Talib, PhD
Assoc. Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

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

Date: 8 Jun 2009

DECLARATION

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

NOOR JAWAD RIDHA

Date: 20 May 2009

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

ΔL	Change in length.
ΔT	Change in temperature.
λ	Thermal conductivity
β	Adjustable parameter of the energy pulse
ω	Angular frequency
ρ	Density
τ	Pulse time
Δ	Sampling rate
α	Thermal diffusivity
α_c	Corrected value of thermal diffusivity
σ_o	DC contribution.
$\partial T/\partial x$	Temperature gradient
α_x	Thermal diffusivity calculated at x percent rise
A	Surface area
Å	Angstrom unit
C	Capacitance
C_o	Capacitance of the empty system
c_p	Specific heat capacity
r	Distance between two conducting surfaces
D	Dielectric induction
E	Electric field
$E(\omega)$	Fourier transforms of the time dependent field

f	Frequency
G	Conductance
g	Small depth at the front surface
J_u	Heat flux
K_R	Correction factor for Taylor rising curve data
K_x	Constant corresponding to x% of maximum temperature rise
l	The mean-free path
L	Sample length
L	Sample thickness
P	Polarization
$P(\omega)$	Fourier transforms of the time dependent polarization
Q	Charge accumulated on a surface
Q	Energy of the light pulse
T	Temperature
t	Time
$t_{0.25}$	Time required to reach 25% maximum temperature rise
$t_{0.75}$	Time required to reach 75% maximum temperature rise
$t_{1/2}$, $t_{0.5}$	Time required for the back surface of the sample to reach half the maximum temperature rise
t_a	Time axis intercept of the temperature versus time curve
T_C	Phase transformation temperature (Curie temperature)
t_c	Characteristic rise time
T_M, T_{max}	Maximum temperature rise at the sample rear surface
T_0	Initial temperature at the rear surface of the sample
t_x	Time required to reach x % of T_{Max}
v	Lattice vibration velocity,

V	Applied voltage
$V(\omega)$	Measured voltage
ε	Dielectric constant
$\varepsilon(\omega)$	Dielectric constant as a function of angular frequency
ε^*	Complex dielectric constant as measured by the instrument
$\varepsilon`$	Real dielectric constant
ε_o	Dielectric constant of free space
ε_r	Relative dielectric constant
χ	Electric susceptibility
$\chi`$	Real susceptibility
$\chi``$	Imaginary susceptibility
x	Concentration of Sr^{2+} ions

LIST OF ABBREVIATIONS

SEM	Scanning Electron Microscope
XRD	X-ray Diffraction
Hz	Hertz
AC	Alternating Current
IR	Infra Red
$DRAM_S$	Dynamic random access memories
$MLCC_S$	Multi-Layer Ceramic Capacitors

CHAPTER 1

INTRODUCTION

1.1 Introduction to the Ceramics and its Applications

The term "ceramic" referred to clay-based materials. However, new generations of ceramic materials have expanded the scope and number of possible applications. Ceramic materials are inorganic compounds, usually oxides, nitrides, or carbides. The bonding is very strong either ionic or network covalent. Many adopt crystalline structures, but some form glasses. The properties of the materials are a result of the bonding and structure.

The most important thermal properties of ceramic materials are heat capacity, thermal diffusivity, and thermal conductivity. Many applications of ceramics, such as their use as insulating materials, are related to these properties. Ceramics can withstand high temperature, are good thermal insulators and do not expand greatly when heated. This makes them excellent thermal barriers, for applications such as lining industrial furnaces, thermal paint and covering the space shuttle to conserve it from high temperatures. The last generation of gas turbines hot path components (typically combustion chamber, transition pieces, rotating blades and vanes) are protected against the hot gases (>1300°C) by a ceramic thermal barrier coating (TBC) with a thickness ranging from 300 μm up to 1 or more millimeters (Cernuschi et al., 2004).

Ceramics are strong, hard, and durable and have low densities and high melting points. This makes them attractive structural materials. One significant drawback is their brittleness, but this problem was overcome by the development of new materials as example composites.

Ceramics vary in electrical properties from excellent insulators to superconductors. Thus, they are used in a wide range of applications. Some are capacitors or semiconductors in electronic devices. For example, piezoelectric materials can convert mechanical pressure into an electrical signal and are especially useful for sensors.

In recent years, much attention was devoted to the development of dielectric materials for voltage controlled, frequency-fast phase shifters and filters operating. The development in electronic and related industries on dielectric materials has created the interest to synthesize new materials with suitable properties for industrial requirements (Zhaow, 2006).

One of the electronics which attracted tremendous research interest is $BaTiO_3$ (barium titanate) this material has two crystallographic site, i.e. A and B site and the modification can lead to new materials with different properties (Walter, 2005). Ferroelectrics such as $Ba_{1-x}Sr_xTiO_3$ (barium strontium titanate) have emerged as leading candidates for electronic applications due to their highly nonlinear dielectric