UNIVERSITI PUTRA MALAYSIA

MICROSTRUCTURAL AND DIELECTRIC P ROPERTIES OF (Ba,Nb)(Ti,Cu)03-(BNTC) AND (Ba,Nb)(Ti,Sn)03-(BNTS) CERAMICS

SOMSATHITH KEOPHILAVONG

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By

SOMSATHITH KEOPHILAVONG

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June 2003

Chairman: Professor Abdul Halim Bin Shaari, Ph.D.

Faculty: Science and Environmental Studies.

Microstructural and dielectric studies of $(Ba_{1-x}Nb_x)(Ti_{1-x/2}Cu_{x/2})O_3$ and $(Ba_{1-x}Nb_x)(Ti_{1-x/2}Sn_{x/2})O_3$ prepared by solid-state reaction route were investigated. The compositions with varying x in those systems were prepared by standard powder processing techniques. The two systems were based on the reaction between $BaCO_3$, Nb_2O_5, TiO_2 and CuO to form (Ba,Nb)(Ti,Cu)O_3 (BNTC) and the other system is the reaction between $BaCO_3$, Nb_2O_5, TiO_2 and SnO_2 to form (Ba,Nb)(Ti,Sn)O_3(BNTS). These ceramics compounds are of commercial importance as ceramic capacitors and there is also scientific interest since it provides a straightforward example of the effect of solid solution composition of ceramics on dielectric properties. This thesis reports the detailed investigation with respect to the above mentioned compositions. The variation of microstructure with sintering temperature and soaking time at each sintering temperature, and that in the capacitance and resistance of each of the sample has been examined.

The results of X-ray diffraction revealed lattice parameter changes of $BaTiO_3$ after substitution of Nb^{3+}, Cu^{2+} and Sn^{3+}. The graph of all compositions with x in these systems while sintering at 1250°C for 4 hours and at 1300°C for 2 hours of both systems were almost similar. It is found that in the entire composition range (0.01 x 0.09) the structures were almost tetragonal. Microstructural and dielectric properties of these systems have been studied. Microstructural investigations by SEM studies showed the presence of domains with small grains size. The average grain size was about 0.5 - 2 μm. Dielectric constant (*K*) and dielectric loss (*D*) were measured and correlated with the density and microstructure. Dielectric properties of these composites were measured as functions of frequency. The values of dielectric constant were found to be in the range 80-100. The values of loss tangent were small. The use of combined impedance and electric modulus spectroscopy to characterize electroceramics was briefly reviewed. This approach has several advantages over dc measurements and conventional impedance complex plane plot and allows electrical heterogeneities associated with surface layers, inner and outer regions of individual grains and grain boundary-dominated phenomena to be probed.

Abstrak tesis yang dikemukakan kepada senat Universiti Putra Malaysia bagi memenuhi keperluan ijazah Master Sains

SIFAT MIKROSTRUKTUR DAN DIELEKTRIK BAGI SERAMIK (Ba,Nb)(Ti,Cu)O_3-(BNTC) DAN (Ba,Nb)(Ti,Sn)O_3-(BNTS)

Oleh

SOMSATHITH KEOPHILAVONG

Jun 2003

Pengerusi: **Profesor Abdul Halim Bin Shaari, Ph.D.**

Fakalti: **Sains dan Pengajian Alam Sekitar**

Kajian mikrostruktur dan dielektrik bagi $(Ba_{1-X}Nb_X)(Ti_{1-X/2}Cu_{X/2})O_3$ dan $(Ba_{1-X}Nb_X)(Ti_{1-X/2}Sn_{X/2})O_3$ yang disediakan melalui teknik tindakbalas keadaan pepejal telah dijalankan. Komposisi dengan nilai x yang berbeza telah disediakan dengan teknik piawai proses hablur. Dua sistem seramik disediakan. Satu sistem terdiri daripada tindakbalas di antara $BaCO_3$, Nb_2O_5, TiO_2, CuO dan sistem kedua terdiri daripada $BaCO_3$, Nb_2O_5, TiO_2, SnO_2. Bentuk seramik bagi kedua sistem ini mempunnyai nilai komersial sebagai kapasitor seramik dan juga mempunyai kepentingan saintifik kerana ini memberikan satu contoh yang baik tentang kesan komposisi pepejal terhadap sifat dielektrik. Tesis ini melaporkan satu kajian berkaitan dengan komposisi-komposisi di atas. Perubahan mikrostruktur dengan suhu persinteran dan masa persinteran setiap suhu, dan perubahan kapasitan dan rintangan setiap sampel telah dikaji.

Hasil daripada belauan sinar-X menunjukkan perubahan parameter kekisi $BaTiO_3$ bila terjadi penggantian Nb^{+3}, Cu^{+2}, dan Sn^{+3}. Graf bagi semua nilai x di dalam sistem yang telah disinter pada suhu 1250°C selama 4 jam dan sistem yang disinter pada suhu 1300°C selama 2 jam adalah hampir sama. Didapati bahawa di dalam seluruh julat komposisi (0.01 x 0.09) struktur sampel adalah tetragon. Mikrostruktur dan sifat dielektrik telah dikaji. Kajian mikrostruktur dengan menggunnakan Mikroskop Imbasan electron menunjukkan domain-domain dengan butiran bersaiz kecil. Purata saiz butiran adalah 0.5-2 μm. Pemalar dielektrik (*K*) dan faktor kelesapan dielektrik (*D*) telah diukur dan dikaitkan dengan ketumpatan dan mikrostruktur. Sifat dielektrik komposit-komposit diukur sebagai fungsi frekuensi di antara 10^{-2} hingga 10^{6} Hz. Nilai pemalar adalah di adalam julat 80-100. Nilai kelesapan dielektrik adalah kecil.

Satu ringkasan penggunaan gabungan spektroskopi impedans dan modulus elektrik untuk mencirikan elektroseramik telah diberi. Teknik ini mempunyai kelebihan berbanding denagn pengukuran arus terus dan pemplotan impedans di dalam satah kompleks, kerana teknik ini membolehkan ketakhomogenan elektrik yang berkaitan dengan lapisan permukaan kawasan dalaman dan luaran setiap butiran dan fenomena yang berkaitan dengan keadaan sempadan butiran dikaji.

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ways has continuously provided me with love and inspiration. He patiently tolerated my preoccupation with my studies and work. My special love is to him.

I certify that an Examination Committee met on 5th June 2003 to conduct the final examination of Somsathith Keophilavong on his Master of Science thesis entitled "Microstructural and Dielectric Properties of (Ba,Nb)(Ti,Cu)O_3-(BNTC) and (Ba,Nb)(Ti,Sn)O_3-(BNTS) 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:

ZAIDAN ABDUL WAHAB, Ph.D.
Faculty of Science and Environment Studies
Universiti Putra Malaysia
(Chairman)

ABDUL HALIM SHAARI, Ph.D.
Professor
Faculty of Science and Environment Studies
Universiti Putra Malaysia
(Member)

WAN MOHD DAUD WAN YUSOFF, Ph.D.
Associate Professor
Faculty of Science and Environment Studies
Universiti Putra Malaysia
(Member)

JAMIL BIN SURADI, Ph.D.
Associate Professor
Faculty of Science and Environment Studies
Universiti Putra Malaysia
(Member)

GULAM RUSUL RAHMAT ALI, Ph.D.
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 14 JUL 2003

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

ABDUL HALIM SHAARI, Ph.D.
Professor
Faculty of Science and Environment Studies
Universiti Putra Malaysia
(Chairman)

WAN MOHD DAUD WAN YUSOFF, Ph.D.
Associate Professor
Faculty of Science and Environment Studies
Universiti Putra Malaysia
(Member)

JAMIL BIN SURADI, Ph.D.

Associate Professor
Faculty of Science and Environment Studies
Universiti Putra Malaysia
(Member)

AINI IDERIS, Ph.D.
Professor/Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 15 2003

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.

Somsathith KEOPHILAVONG

Date : 25-06-03

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

λ	Wave Length
a, b, c	Lattice Parameters
d_{hkl}	Reciprocal d Vector
hkl	Miller Indices
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
f, ω	Frequency and Angular Frequency
A	Cross Sectional Area
θ	Bragg Angle
$\tan\delta$	Loss Tangent
PVA	Polyvinyl Alcohol
T	Absolute Temperature (Kelvin)
TCK	Temperature Coefficient of Dielectric
K	Dielectric
C_p	Capacitor
G_p	Conductor
logf	Logarithm of Frequency
logC	Logarithm of Capacitance
C	Capacitance
Tc	Critical Temperature
p	Pressure
t	Time

Å	Angstrom Unit
D	Diffusivity
$\beta_{1/2}$	Full Width Half Maximum
I	Current
j	=√-1
τ	Relaxation Time (sec)
ε_o	Permittivity of Vacuum
ε_r	Relation Permittivity
V	Applied Voltage
Z	Impedance
Z'	Real part of Admittance
Z"	Imaginary Part of Impedance
Z*	Complex Impedance
M	Modulus
M'	Real part of Modulus
M"	Imaginary Part of Modulus
M*	Complex Modulus
LP/CPA	Lumped Parameter/Complex Plane Analysis
ρ	Density
m	Mass
Ac	Alternating Current
Dc	Direct Current

CHAPTER I

INTRODUCTION

Relevance and Importance of Dielectric Ceramics

Ceramics materials are polycrystalline, inorganic materials which consist of metallic and nonmetallic elements bounded together primarily by ionic and / or covalent bonds. The chemical composition of ceramic materials varies considerably, from simple compounds to mixtures of many complex phases bonded together. The earliest use of ceramics was in pottery and bricks, Koller (1994).

The properties of ceramic materials also vary due to differences in bonding. In general, ceramic materials are typically hard and brittle with low toughness and ductility. Ceramic units with even higher capacitance to volume ratios have been made possible by utilizing the readiness with which barium titanate can be converted from an insulator to a conductor and vice versa.

Ceramic dielectrics are produced in a wide range of compositions and shapes to cover the applications to which they are better adapted than alternative materials, Herbert (1992).

Ceramics are usually good electrical and thermal insulators due to the absence of conduction electrons. They have relatively high melting temperatures and high chemical stability in many hostile environments due to the stability of their strong bonds. In general, ceramics materials used for engineering applications can be divided into groups: traditional ceramic materials, made from three basic compounds [Clay, Silica (SiO_2), and Feldspar ($K_2OAl_2O_3.6SiO_2$)], such as bricks, and engineering ceramic materials which are pure or nearly pure compounds, such as alumina (Al_2O_3), Silicon carbide (SiC), silicon nitride (ZrO_2) etc, Smith (1996).

The double oxides formed between the oxides of alkaline-earth (AE) metals (M= Ca, Sr and Ba) and those of some of the group IV elements are of great industrial and technological importance. For instance, the AE carbonates are the well-known precursors to innumerable inorganic synthesis and reactions, while AE silicates are of relevance and direct bearing in the slag chemistry of industrials production of iron and steels. Similarly, the discovery of superconductivity in 'copper-free' cubic perovskite systems such as $BaPb_{1-x}Sb_xO_3$ (T_c= 3.5 K at x=0.25) and $BaPb_{1-x}Bi_xO_3$ (T_c = 13 K at x = 0.3), Nagarajan *et al*. (1991) has triggered much activity in the pseudobinary alkaline earth oxide-PbO (PbO_2) system. In addition the technological impact of closely structure-related titanate ($MTiO_3$) of the alkaline-earth metals is too great to be overlooked. For example $SrTiO_3$ is as well known varistors and $BaTiO_3$ is a ferroelectric and piezoelectric material with a variety of application.

The structure of a barium titanate ($BaTiO_3$) crystal depends on the temperature. Above its Curie point, T_c (approximately 130°C), the unit cell is cubic and nonpolar. Below the Curie point, the structure is slightly distorted to the tetragonal form with dipole moment in the (001) direction, Pakokthom *et al.* (1999). In consideration of work carried out regarding the effect of particle size of approximately 0.1 μm.

Barium titanate is known as a typical ferroelectric material with three phase transitions: a ferroelectric-paraelectric phase transition (cubic-tetragonal) around 130°C (also called Curie temperature T_c), a tetragonal-orthorhombic phase transition around 5°C and an orthorhombic-rhombohedral phase around -80°C. $BaTiO_3$ based solid solutions have been a subject of extensive studies since the early 1950s, Liqin zhou *et al.* (2001).

With no doubts $BaTiO_3$ is one of the most studied ferroelectric materials. Actually, the discovery of the ferroelectricity was done independently in various countries during the World War II, Von hippel (1950) just in $BaTiO_3$ crystal. The reason of numerous investigations on $BaTiO_3$ is its remarkable properties in the tetragonal phase. It also has a high dielectric constant at ambient temperature, Balzar *et al.* (1999). This ceramic material shows piezoelectric properties as well. Another important features are its chemical and mechanical stability in a wide temperature range, which facilitates its fabrication in bulk polycrystal and both epitaxial and polycrystalline thin films. All of these properties make this ceramic very useful in different applications such as dynamic random-access memories, piezoelectric transducers, thermistors and actuators.

Research conducted over the past year at the Ohio State University has demonstrated that $BaTiO_3$ can be produced from solid metallic precursor. Elemental Barium and titanium are first blended together in an equimolar ratio and then milled to produce a Ba-Ti precursor powder. The powder is packed into a noble metal tube, which is sealed and deformed into a dense tape. The tape is then heat treated so as to transform the metallic precursor core into dielectric $BaTiO_3$, Sandhage *et al*. (1993).

Dielectric Analysis

Impedance Analysis is a powerful non-destructive tool for analyzing a range of electroceramic materials. The advantages of this technique are that it yields accurate and repeatable results, which are unobtainable by other electrical means. The properties of ceramic materials depend on close control of their structure in terms of composition, ceramic texture, and dopants present. Electrical analysis allows the complexities of these materials to be discovered by utilizing the frequency dependence of the individual components. A variety of solid state parameters can be monitored including, electrical homogeneity, electrode/electrolyte interfaces, surface layers, ferroelectric properties, temperature coefficients related to resistive behaviour and bulk/grain boundary effects.

Furthermore, dielectric analysis is also a powerful non-destructive tool for characterizing materials; it can provide accurate, repeatable results unavailable by other electrical means. The electrical properties of a material are unique and can be discovered by utilizing the frequency dependence of its constituent components. In addition, the study of frequency related phenomena, as a function of applied bias or temperature is often essential in the performance testing of materials.

Direct current or alternating current measurements at a fixed frequency place severe limitations on the amount of information that can be derived from them. However, with the advent of computers and multifrequency analyzes, there is a lot more information that can be derived from the equipment normally used to determine their dielectric constant alone, Gerhardt (1998).

Dielectric materials are insulators as they have a large energy gap between the valence and conduction bands. Thus, the electrons in the valence bands cannot jump to the conduction band. Therefore, the resistivities of these materials are very high. Most ceramics are dielectric materials and have a mixture of ionic and covalent bonding. Although these materials do not conduct electric current when an electric field is applied, they are not inert to the electric field. The field may cause a slight shift in the balance of charge within the material to form an electrical dipole. Thus, the material is called a " dielectric" material.

The dielectric properties of $BaTiO_3$ ceramics are associated with its microstructure, which depends on the stoichiomteric ratio, dopant nature and ceramic processing. One of the most important applications of $BaTiO_3$ based ceramics is the fabrication of multilayer capacitors.