UNIVERSITI PUTRA MALAYSIA

MICROSTRUCTURES AND DIELECTRIC PROPERTIES OFPb (Al,Vl-,)Ohs SYSTEMS

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MICROSTRUCTURES AND DIELECTRIC PROPERTIES OF $Pb(Al_xV_{1-x})O_{3\pm\delta}$ SYSTEMS

By

WALTER CHARLES PRIMUS

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
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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 Master of Science

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

Faculty: **Science**

The microstructures and electrical properties of $Pb(Al_xV_{1-x})O_{3\pm\delta}$ ceramic have been investigated. The samples were prepared using solid-state technique and were sintered at 800 °C, 850 °C and 900 °C. Surface morphology studies show that small grains with submicron size ~ 0.25 μm coexist with the bigger grains in micron size. As the sintering temperature increased, the grains size increase and thus become more compact. From XRD analysis, the sample structure obtained is an orthorhombic system with space group PMMA and unit cell volume is 469.595 $Å^3$.

The dielectric constant, ε' for sample PAV 7/800, PAV 7/850 and PAV 7/900 increased as the sintering temperature increased where the values of ε' for sample sintered at 900 °C is ~ 6000 at 10^{-2} Hz and ~ 90 at 1 kHz. However, the loss factor, ε'' for sample sintered at 900 °C is higher than that of other samples. The loss tangent, $\varepsilon''/\varepsilon'$ for sample PAV 7/800, PAV 7/850 and PAV 7/900 at 1 kHz are 0.1, 0.12 and 0.16 respectively. The PAV 0.9 shows the highest ε' ~4000 at 10^{-2} Hz but the ε'' for this sample is also high. This is followed by sample PAV 0.7 and PAV 0.3. Between frequencies higher than 1 kHz, the magnitudes of the ε' data dispersion (~

80) are similar for samples PAV 0.3, PAV 0.7 and PAV 0.9. At 10^{-2} Hz to 1 kHz, the dispersion of ε' is strongly dependent on frequency. However, the ε' dispersion is independent with frequency at 1 kHz to 10^5 Hz. The mechanisms that are observed from all samples are quasi dc, dipolar and barrier layer. A peak observed at 10^2 Hz is due to the ionic relaxation processes. The activation energy that is obtained from sample PAV 7/800 is 0.416. It indicates that the electrons hopping are weak. An equivalent circuit model has been proposed to represent the mechanism observed.

The conductivity, σ_{ac} is increased from $3.0\text{x}10^{-8}$ to $8.0\text{x}10^{-8}$ mho/m for sample PAV 7/800 and PAV 7/900 respectively. For other samples with different Al composition, σ_{ac} increased from $1.0\text{x}10^{-9}$ to $1.0\text{x}10^{-8}$ mho/m for sample PAV 0.3 and PAV 0.9 respectively. The σ_{ac} curve exhibits two distinct regions where the low frequency region is weakly dependent on frequency due to free charge carriers while the high frequency region is strongly dependent with frequency due to bound charge carriers in this sample. The σ_{ac} is increased from 10^{-9} to 10^{-6} mho/m for 50 °C and 200 °C respectively. The activation energy of sample PAV 7/800 and PAV 0.1 is ~0.65 eV and may be due to the ac conduction in terms of hopping transport of charge carrier in a narrow band of localization states as the Fermi level.

In complex impedance plots, only one semicircle is observed at low frequency and does not started from the origin due to the high frequency resistance effect. For sample PAV 7/800, the resistance obtained from the plot is $8.99\text{x}10^9$ ohm/m and the value of the capacitance is $1.5\text{x}10^{-10}$ F. The capacitance value obtained is in the range of bulk ferroelectric mechanism. In direct current measurement, the curve obtained obeyed the Ohm's law and the activation energy increased from 0.85 eV to 1.15 eV as the sintering temperature increases from 800 °C to 900 °C and 0.71 eV to 1.62 eV when Al compositions increase from PAV 0.1 to PAV 0.9.

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

MICROSTRUKTUR DAN SIFAT DIELEKTRIK BAGI SISTEM $\mathbf{Pb(Al_xV_{1-x})O_{3\pm\delta}}$

Oleh

WALTER CHARLES PRIMUS

April 2005

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

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Mikrostruktur dan sifat elektrik bagi ceramik $\mathrm{Pb(Al_xV_{1-x})O_{3\pm\delta}}$ telah dikaji. Sampel tersebut disediakan menggunakan teknik keadaan pepejal dan disinter pada 800 °C, 850 °C dan 900 °C. Kajian morfologi permukaan menunjukkan butiran kecil bersaiz submikron ~0.25 μm wujud bersama dengan butiran besar bersaiz mikron. Peningkatan suhu sinteran menyebabkan saiz butiran bertambah besar dan seterusnya menjadi lebih padat. Daripada analisis XRD, struktur sampel ialah sistem orthorhombik dengan kumpulan ruang PMMA dan isipadu sel unit 469.595 Å^3.

Pemalar dielektrik, ε' bagi sampel PAV 7/800, PAV 7/850 dan PAV 7/900 meningkat dengan peningkatan suhu sinteran di mana nilai ε' bagi sampel yang disinter pada 900 °C adalah ~ 6000 pada 10^{-2} Hz dan ~ 90 pada 1 kHz. Walau bagaimanapun, faktor kehilangan, ε'' bagi sampel disinter pada 900 °C adalah tinggi berbanding sampel yang lain. Nilai bagi kehilangan tangen, $\varepsilon''/\varepsilon'$ bagi sampel PAV 7/800, PAV 7/850 dan PAV 7/900 masing-masing adalah 0.1, 0.12 dan 0.16 pada 1kHz. Sampel PAV 0.9 menunjukan nilai tertinggi ε' ~4000 pada 10^{-2} Hz tetapi ε'' bagi sampel ini juga tinggi. Ini diikuti oleh sampel PAV 0.7 dan PAV 0.3. Pada friquensi tinggi daripada 1 kHz, magnitud bagi taburan data ε' (~ 80) adalah sama untuk sampel PAV 0.3, PAV 0.7 dan PAV 0.9. Diantara 10^{-2} Hz hingga 1 kHz, taburan ε' sangat bergantung pada frequensi. Walau bagaimanapun, taburan ε' tidak bergantung pada frequensi pada 1 kHz hingga 10^{5} Hz. Mekanisme yang diperolehi daripada semua sampel ialah quasi dc, dwikutub dan lapisan halangan. Puncak yang didapati pada 10^{2} Hz adalah disebabkan oleh proses relaksasi ionik. Tenaga pengaktifan yang diperolehi daripada sampel PAV 7/800 ialah 0.416 eV. Ini menunjukan bahawa loncatan elektron adalah lemah. Model litar setara telah dicadangkan untuk mewakilkan mekanisme yang diperolehi.

Peningkatan konduktiviti, σ_{ac} daripada $3.0\text{x}10^{-8}$ kepada $8.0\text{x}10^{-8}$ mho/m bagi sampel masing-masing PAV 7/800 dan PAV 7/900. Bagi sampel yang lain dengan komposisi Al berbeza, peningkatan σ_{ac} dari $1.0\text{x}10^{-9}$ kepada $1.0\text{x}10^{-8}$ mho/m bagi sampel masing-masing PAV 0.3 dan PAV 0.9. Lengkok σ_{ac} juga menunjukan dua bahagian di mana bahagian frequensi rendah bergantung secara lemah pada frekuensi disebabkan oleh pembawa cas bebas manakala bahagian frekuensi tinggi sangat bergantung pada frekuensi disebabkan oleh pembawa cas terikat dalam sampel ini. σ_{ac} meningkat daripada 10^{-9} kepada 10^{-6} mho/m masing-masing dan bagi 50 °C dan 200 °C. Tenaga pengaktifan bagi sampel PAV 7/800 dan PAV 0.1 ialah pada ~0.65 eV dan ini mungkin disebabkan oleh kekonduksian ac bagi pengangkutan loncatan oleh pembawa cas dalam jalur tenaga yang sempit bagi keadaan setempat seperti paras Fermi.

Dalam plot impedant komplex, terdapat satu semi-bulatan diperolehi pada frequenci rendah dan tidak bermula daripada asalan disebabkan oleh kesan rintangan frequensi

tinggi. Bagi sampel PAV 7/800, rintangan yang diperolehi daripada plot tersebut ialah 8.99x10^{9} ohm/m dan nilai kapasitan ialah 1.5x10^{-10} F. Nilai kapasitan yang dicerap ialah di dalam julat mekanisme ferroelektrik. Dalam pengukuran arus terus, data yang diperolehi mematuhi hukum Ohm dan tenaga pengaktifannya meningkat daripada 0.85 eV kepada 1.15 eV apabila suhu sinteran meningkat dari 800 ^{o}C kepada 900 ^{o}C dan 0.71 eV kepada 1.62 eV apabila komposisi Al bertambah dari PAV 0.1 kepada PAV 0.9.

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LIST OF SYMBOLS AND ABBREVIATIONS

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
μ	Micron
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
j	$=\sqrt{-1}$
k	Boltzmann constant
kHz	Kilohertz
In	Natural logarithm

log	Logarithm
mHz	Milihertz
∝	Proportional to
→	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	Activation energy
EDX	Electron Dispersion X-ray
G	Conductance
Hz	Hertz
I	Current
Im	Imaginary part
K	Kelvin
M	Modulus
M*	Complex modulus
M′	Real part of modulus
M″	Imaginary part of modulus
MHz	Megahertz

R	Resistance
Re	Real part
SEM	Scanning electron microscope
T	Absolute temperature (Kelvin)
TGA	Thermo Gravimetric Analysis
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

Dielectric is a field of knowledge that belongs to physics, chemistry, biology and engineering. Dielectrics are not confined to the narrow area of insulators, but to any non-metal that interacts with electric or electromagnetic fields. Polarization and the dynamics of electric charges are at the heart of dielectrics. These are often described in terms of macroscopic properties such as permittivity, dielectric loss and also dielectric constant. Electrical engineers have characterized dielectrics macroscopically using field vectors, equivalent circuits and reliability statistics. In contrast, the physicist and chemist have pushed forward the understanding of dielectric response in terms of molecular and structural response and relaxation. Many of the fundamental problems have now been addressed and it is now possible to move from dielectric analysis to dielectric synthesis. This is of considerable interest to most areas of science and demonstrates the cross-disciplinary nature of dielectrics.

Not only the electrical property has been investigated but also its correlation on chemical and microstructure. Scanning Electron Microscope (SEM), Energy Dispersive Microanalysis (EDS) and X-ray diffraction (XRD) are used in hundreds of applications where knowledge of chemical information on the micro- or nanoscale is important. Major users include industry, university research institutes and government facilities. Typical applications are in materials research, quality control, failure analysis, and forensic science. Industries that commonly use this technique include: semi-conductor and electronics, metals, ceramics, minerals, manufacturing, engineering, nuclear, paper, petroleum, bio-science, and the motor industry.

The development in electronic and related industries on dielectric materials has pushed researchers to synthesize new materials with good dielectric properties. From ABO_3 perovskite structure (ca. $BaTiO_3$) to the modification on the A and B sites, a new material with good electrical and mechanical properties has been found. Recent work has shown that the substitution on A site with Pb and some modification on B site produce a good result on its dielectric and mechanical properties. Many works have been reported on the effect of substitution and modification on B site. However substitution and modification with aluminium (Al^{3+}) and vanadium (V^{5+}) on B site have not been reported yet. In this work, the $Pb(Al_xV_{1-x})O_{3\pm\delta}$ ceramic systems has been studied and its electrical properties have been characterized.

1.2 Objective

The main objectives of this study is to characterize the $Pb(Al_xV_{1-x})O_{3\pm\delta}$ ceramic systems by TGA, XRD, SEM, EDX, dielectric spectrometer and dc conductivity measurement. A detail objective of this study was conducted in order to investigate: