SYNTHESIS AND CHARACTERIZATION OF $BaTiO_3$ PELLETS AND THIN FILMS

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by

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscope
Ba	Barium
$BaCO_3$	Barium carbonate
BaO	Barium oxide
Ba_2TiO_4	Barium orthotitanate
$BaTiO_3$	Barium titanate
Ba : Ti	Barium to titanium ratio
BT	Barium titanate
CMY	Cyan, Magenta, and Yellow color
CIJ	Continuous Inkjet
DOD	Drops on Demand
DTG	Differential Thermalgravimetric
EPD	Electrophoretic
FWHM	Full Width at Half Maximum
IS	Impedance Spectroscopy
PAA	Polyacrylic Acid
PIJ	Piezo Inkjet

PLD	Pulse Laser Deposition
PTC	Positive Temperature Coefficient
Ra	Surface Roughness
RGB	Red, Green, and Blue color
SEM	Scanning Electron Microscope
TGA	Thermal gravimetric Analysis
Ti	Titanium
TiO_2	Titanium dioxide
Ti $(CH_3CH_3CHO)_4$	Titanium isopropoxide
XRD	X-Ray Diffraction

LIST OF SYMBOLS

A	Area
C	Capacitance
D	Thickness
d	Spacing between planes
E	Total Voltage
F	Force
f	Frequency
Hz	Hertz
I	Current
M	Molarity
MHz	Megahertz
MPa	Megapascal
N	Newton
P	Pressure
Q	Electrical charge can be stored
R	Resistance
V	Applied voltage

Z	Impedance
$^{\circ}C$	Degree Celsius
ε_0	Permittivity (dielectric constant) of a vacuum
ε	Dielectric constant of material
Π	Pi
µ	Micron
ω	Omega
λ	Wave length
Ω	Ohm
Θ	Theta
β	Full width half maximum of peak
βo	Instrumental peak broadening

Sintesis dan Pencirian Pelet dan Filem Nipis $BaTiO_3$

ABSTRAK

Barium titanat telah disintesiskan dengan pendekatan kaedah keadaan pepejal dan akueus. Sintesis keadaan pepejal digunakan untuk menyediakan pelet barium titanat dengan menggunakan kaedah metalurgi serbuk. Barium karbonat dan titanium dioksida dicampurkan bersama dalam jumlah yang sesuai di dalam lesung batu akik. Pelet barium titanat dicampurkan berdasarkan 5 nisbah Ba/Ti yang berbeza iaitu 1:0.9, 1:0.95, 1:1, 1:1.05, 1:1.1. Pelet telah disinterkan di udara pada suhu 1400 °C. Filem nipis barium titanat disediakan dengan kaedah akueus. Sol-gel barium titanat disediakan berdasarkan nisbah yang sama dengan pelet. Filem nipis sol-gel barium titanat telah disadur di atas substrat kaca menggunakan pencetak berkomputer dan dibakar pada 400 °C. Pelet dan filem nipis kedua-duanya dicirikan dengan menggunakan pembelaun sinar-X, mikroskop pengimbas elektron, mikroskop daya atom (filem nipis sahaja), dan spektroskopi galangan. Fokus tesis ini adalah menentukan ciri-ciri dielektrik barium titanat termasuk rintangan, kapasitan, pemalar dielektrik, frekuensi pengenduran, dan tangen kehilangan. Ketumpatan tertinggi untuk barium titanat pelet adalah 5.90 g/cm^3 iaitu apabila Ba:Ti adalah 1:1 digunakan. Purata ketebalan filem nipis adalah 2.89 nm seperti yang diukur oleh mikroskop daya atom dan disahkan oleh mikroskop pengimbas electron. Ciri-ciri barium titanat telah diperhatikan dalam suhu yang berbeza-beza bermula dari suhu bilik sehingga ke 450 °C (untuk pelet) dan 300 °C (untuk filem nipis). Pemalar dielektrik untuk pelet telah diukur pada 10 kHz (suhu bilik) adalah berbagai-bagai dari maksimum iaitu 2810 sehinggalah paling minimum iaitu 1375. Sampel dengan nisbah Ba:Ti 1:1 menunjukkan nilai pemalar dielektrik yang tertinggi. Nilai pemalar dielektrik yang tertinggi diukur pada 100 °C iaitu pada sampel stoikiometri. Keputusan pembelauan sinar-X menunjukkan pembentukan fasa kedua, Ba_2TiO_4 apabila lebihan barium sebanyak 5 % dan 10 % ditambah. Filem nipis barium titanat menunjukkan kehabluran yang rendah berbanding pelet. Pengukuran kelebaran puncak pembelauan sinar-X pada filem nipis menunjukkan purata saiz hablur adalah 14 nm berbanding pelet iaitu 110 nm. Spektroskopi galangan barium titanat pelet menunjukkan kehadiran komponen rintangan sempadan butir, komponen konduksi butir, dan juga komponen ketiga feroelektrik. Kehadiran komponen yang berkenaan ini disahkan melalui plot “Curie Weiss”. Filem nipis barium titanat tidak menunjukkan kehadiran komponen feroelektrik. Pemalar dielektrik pelet (ε= 2810) adalah jauh lebih tinggi berbanding dengan pemalar dielektri filem nipis (ε = 342) dan ini disebabkan oleh kehabluran yang rendah pada filem nipis

Synthesis and Characterization of $BaTiO_3$ Pellets and Thin Films

ABSTRACT

Barium titanate was synthesized using a solid state approach and an aqueous method. Solid state syntheses were used to prepare barium titanate pellets using a powder metallurgy method. Appropriate amounts of barium carbonate and titanium dioxide powder were mixed together in an agate mortar. Barium titanate pellets were mixed according to 5 different ratios of Ba/Ti which are 1:0.9, 1:0.95, 1:1, 1:1.05, 1:1.1. Pellets were sintered in air at a temperature 1400 °C. Barium titanate thin films were prepared using an aqueous method. Sol-gel of barium titanate was prepared according to the similar ratios as pellets. Thin films of barium titanate sol-gel were deposited using a desktop printer onto a glass substrate and fired at 400 °C. Both pellets and thin films were characterized by X-ray diffraction, scanning electron microscope, Atomic Force Microscope (thin films only), and impedance spectroscopy. This thesis focuses on determination of dielectric properties of barium titanate including the resistance, capacitance, dielectric constant, relaxation frequency, and loss tangent. The highest density for the barium titanate pellets were 5.90 g/cm^3 when a Ba:Ti ratio of 1:1 was used. The average thicknesses of the thin films were 2.89 nm as measured using the atomic force microscope and verified using the scanning electron microscope. Characteristic of barium titanate were observed under various temperatures starting from room temperature up to 450 °C (for pellets) and 300 °C (for thin films). The measured dielectric constant of the pellets at 10 kHz (at room temperature) varied from a maximum of 2810 to a minimum of 1375. Samples with Ba:Ti ratio of 1:1 show the highest dielectric properties. The highest dielectric constant was measured at 100 °C for stoichiometric samples. X-ray diffraction result shows the production of a secondary phase, Ba_2TiO_4 when barium excess of 5 % or 10 % was added. The barium titanate thin films showed lower crystallinity than the pellets. X-ray diffraction peak broadening measurements of the thin films show an average crystallite size of 14 nm compared to 110 nm for the pellets. Impedance spectroscopy of the barium titanate pellets show the presence of a resistive grain boundary component, a conductive bulk component as well as a ferroelectric third component. The presence of these components were verified via Curie Weiss plots where applicable. The barium titanate thin films did not show the presence of the ferroelectric component. The dielectric constant of the pellets (ε= 2810) were significantly higher than the dielectric constant of the thin films (ε = 342) and this was attributed to the lower crystallinity of the thin films.

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DECLARATION OF THESIS

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CHAPTER 1

INTRODUCTION

1.1 Background

Barium titanate (BT) is a type of dielectric material can be produced by firing a mixture of barium carbonate ($BaCO_3$) and titanium dioxide (TiO_2) in a high temperature. However, inappropriate mixing ratios or firing temperatures may cause the existence of other phases which lower the properties of BT. This research tries to evaluate the effects of Ba:Ti ratio and sintering temperatures on the dielectric properties of BT using impedance spectroscopy (IS).

BT can also be fabricated in the form of thin film. Thin film is the act of applying a thin film to a surface of a substrate with a very thin layer (few nanometers). Thin film deposition is divided into two techniques which are physical technique and chemical technique. However to fabricate a thin film by the physical technique is very costly where the vacuum system is needed, leaving the chemical technique. Until now, the chemical technique of leaving the solution deposition onto the substrate is also costly. To overcome this problem, inkjet printer is an alternative solution to fabricate a thin film of BT with a lower cost. This research aims to compare between the BT pellets and thin films produced by inkjet printer.

1.2 Problem Statement

BT one of the best material to produce a dielectric component because this material has a high dielectric constant. However, it is not easy to produce pure BT. Until now, people had a challenge to produce a pure BT because there has an existence of other phases during the production of BT. This phenomenon will affect the dielectric constant and also the cost of production will be higher. So, to overcome this problem, the optimum ratio between the raw material which is barium and titanium should be identified to ensure the reaction between these two kinds of compound is homogeneous where the pure of BT is produced without existence of any unwanted phases. Hence, in this thesis the ratio between barium and titanium were manipulated starting from an excess of barium ratio, followed by an excess of titanium ratio, and lastly the ratio between barium and titanium equal 1:1. Sintered BT having dense and fine grain microstructure shows better performance. Therefore, nowadays enormous efforts have been devoted to develop a powder synthesis which produces well crystallized BT particles with suitable particle size and morphology.

The stoichiometry between barium and titanium plays important role in the production of high quality of ferroelectric BT. Previous researchers state that the stoichiometry between barium and titanium give an effect to the dielectric properties of BT (W. P. Chen et al., 2008). The excessive of barium or titanium will influence to the production of secondary phase which is Ba_2TiO_4 and $Ba_2Ti_5O_{12}$. The effect of stoichiometry also will change the microstructure and density of BT (Erkalfa et al., 2003). It is important to know the stoichiometry of BT in order to produce a high quality of ferroelectric BT.

Basically, BT has 4 different structures which is rhombohedral, orthorhombic, tetragonal, and cubic where this structure will change depending on temperatures. Every structure will show different dielectric properties. Khatri et al. state the dielectric properties of ceramic will change when different temperatures was applied (2008). The resistivity of ceramic was decrease with the increasing of temperature. It is very important to study and clearly understand the characteristic of BT in the various temperatures condition in order to use this kind of material in an appropriate condition.

In the past decade, BT has been produced by a solid-state which is mixing between $BaCO_3$ and TiO_2 at temperature above 900 °C. However, the microstructure produced by this method has not meet the electronic applications requirement because the production of BT is not enough fine and lack of uniform (Hu et al., 2000). Furthermore, this solid-state technique used a high temperature and certainly using the high cost of processing. So, new alternative technique is needed to overcome this problem where the cost to fabricate a thin film of BT should be cheaper. The sol-gel technique provides big approaches to produce inorganic polymer and organic-inorganic hybrid materials (Kumar et al., 2008). The purpose of using sol-gel technology historically has been mentioned in the middle of 1800's and Schoot Glass Company (Jena, Germany) use this technology for a year later (Brinker & Scherer, 1990). In this method, there can be extraordinary conditions where this sol-gel method can be used to produce products of various shapes, sizes and formats (e.g. films, fibers, monoliths and monosized particles). This technology then developed in many applications of new materials for catalyst (Schubert, 1994), membranes (Brinker et al., 1995), fibers (Zeng et al., 2001), chemical sensors (Wolfbeis et al., 1996), optical gain media (Gvishi et al., 1997), linear applications and photochromic (Levy & Eszquivias, 1995) and solid state electrochemical devices (Dunn et al., 1994). Also wide applications in engineering and