EFFECT OF DIFFERENT PYROLYSIS AND ANNEALING TEMPERATURE ON STRUCTURAL AND ELECTRICAL PROPERTIES OF $K_{0.5}Na_{0.5}(NbO)_3$ THIN FILM

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This report is submitted in accordance with requirement of the University Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

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It is hereby that all the materials in this thesis entitled "Effect of Different Pyrolysis and Annealing Temperature on Structural and Electrical Properties of $K_{0.5}Na_{0.5}(NbO)_3$ Thin Film" are the result of my own work and all the materials that are not the result of my own had been clearly acknowledged in this thesis.

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Date : 22nd June 2017

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment to the requirements for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons). The member of the supervisory is as follows:

……………………………………………………..

(PM Dr Mohd Warikh Bin Abd Rashid)

ABSTRAK

Piezoelektrik seramik filem nipis telah menarik perhatian seluruh dunia untuk menggunakannya dalam aplikasi untuk peralatan elektronik seperti alat pengesan, penggerak dan sebagainya. Namun begitu, bahan yang digunakan iaitu plumbum zirkonia titanate (PZT) tidak bersifat mesra alam kerana mengandungi 60 % plumbum yang boleh mengakibatkan masalah alam sekitar. Oleh itu, untuk menyelesaikan masalah ini, $K_{0.5}Na_{0.5}NbO_3$ (KNN) boleh menjadi sebagai bahan alternatif yang menggantikan PZT. Tujuan kajian ini adalah untuk menyiasat kesan kepada sifat struktur, filem nipis $K_{0.5}Na_{0.5}NbO_3$ (KNN). Dalam eksperimen ini, kaedah sol-gel melalui teknik salutan putaran akan digunakan untuk memfabrikasikan filem nipis KNN. Bahan mentah yang digunakan dalam eksperimen ini adalah natrium acetate, kalium acetate dan niobium penthaethoxide. Ketiga-tiga bahan mentah ini akan dicampur dengan 2-metoxyethanol yang bertindak sebagai pelarut dan acetylacetone akan bertindak sebagai agen pengkelatan untuk mendapatkan sol kepekatan 1.0 M. Seterusnya ,sol akan dilapiskan dengan substrat silikon dan akan diproses melalui salutan putaran pada kelajuan 3000 rpm selama 30 saat sehingga mendapat ketebalan filem yang diinginkan. Selepas itu, filem akan dikalsin pada suhu yang berlainan selama 2 minit dan akan dilindap pada suhu yang berlainan selama 5 minit. Akhir sekali, filem nipis KNN akan dianalisa melalui pembelauan sinar-X (XRD), spektroskopi Raman ,mengimbas electron miskroskopik dan menjalani ujian rintangan untuk mengenal pasti sifat elektrikal dan struktur. Selepas data telah dianalisis, kajian mendapati bahawa suhu memainkan peranan dalam memfabrikasikan filem nipis KNN bagi mendapatkan keputusan yang optimum dan standing dengan sifat-sifat PZT.

ABSTRACT

Piezoelectric ceramic thin film have attracted the worldwide attention to use it for the electronic device applications such as sensor, actuator and etc. However the material used that is lead zirconia titanate (PZT) is not friendly environmental as it is containing 60 % of lead that may cause the environmental problem. To solve the problem, $K_{0.5}Na_{0.5}NbO_3$ (KNN) can be the alternative material to replace PZT. The purpose of this study is to investigate the effect of the different pyrolysis and annealing temperature on the structural properties of $K_{0.5}Na_{0.5}NbO_3$ thin film. In this experiment, sol-gel via spin coating technique is used to fabricate the $K_{0.5}Na_{0.5}NbO_3$ thin film. The raw materials used in this experiment are sodium acetate, potassium acetate and niobium penthaethoxide. These three raw materials will be added with the 2-metoxyethanol as a solvent and acetylacetone as the chelating agent respectively to obtain the 1.0 M sol concentration. Next, the sol will be deposited on the silicon substrate and spin coated at the speed of 3000 rpm for 30 second until the desired thickness of the film is achieved. Then, the thin film will be calcined at the different temperature for 2 minutes and annealed at the different temperatures for 5 minutes. Lastly, the KNN thin film will be analyzed by using the X-ray diffraction, Raman spectroscopy, scanning electron microscopy and resistivity test to determine its electrical and structural properties. After the analysis, it can be concluded that the temperature have affected the fabrication of the KNN thin film in order to get the optimum KNN thin film that comparable to the PZT.

DEDICATION

A big thanks to my beloved father, Chahit anak Jampang and my appreciated mother, Lee Mee Ling and my brothers for giving me continuous support, money, co-operation and understanding in my study.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

PZT	-	Lead zirconia titanate
$PbZrO_3$	-	lead zirconate
$PbTiO_3$	-	lead titanate
˚C	-	Degree celcius
BT	-	barium titanate
MPB	-	morphotrophic phase boundary
BNT	-	bismuth sodium titanate
T_c	-	Curie temperature
WEEE	-	Waste Electrical and Electronic Equipment
KNN	-	potassium sodium niobate
RoHS	-	Hazardous Substances in electrical and electronic equipment
Si	-	Silicon
CH_3COONa	-	Sodium acetate
CH_3COOK	-	potassium acetate
$Nb\ (OC_2H_5)_5$	-	niobium penthaethoxide
$CH_3OCH_2CH_2OH$	-	2-metoxyethanol
XRD	-	X-ray diffraction
SEM	-	Scanning electron microscopy
BLSF	-	bismuth layer structured ferroelectrics
pC/N	-	Pico per newton
E_c	-	coercive field
P_r	-	remnant polarization
TEM	-	transmission electron microscopy

IC	-	Integrated Chip
Na	-	sodium
K	-	potassium
PLD	-	Pulsed laser deposition
ALD	-	atomic layer deposition
CVD	-	chemical vapor deposition
ALE	-	atomic layer epitaxy
μm	-	micrometer
rpm	-	revolution per minute
MOCVD	-	metal organic vapor deposition
cm	-	centimeter
g/mol	-	gram per mol
g	-	gram
N_2	-	nitrogen
nm	-	nanometer
Ωcm	-	Ohm centimeter

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, the studies on piezoelectric materials have been extensively explored due to the rapid development of electronic industries. Piezoelectric materials are the materials that generate electricity due to the applied mechanical stress. Besides that, piezoelectric materials can work in reverse way such as if the electric current is applied, a strain will be generated. Due to the nature of piezoelectric materials itself, makes it is widely used in this electronic industries. The usage of piezoelectric ceramics have been widely used for sensors, actuators, transducers, buzzers and other electronic devices according to Du et al., (2006).

Recently, the popular piezoelectric materials that have been used is lead zirconate titanate or PZT. PZT is a solid solutions between lead zirconate ($PbZrO_3$) which is known as PZ and lead titanate ($PbTiO_3$) known as PT. PZT is widely used in electronic industries because of its excellent piezoelectric properties and commercially available. According to Mohammadi, (2013), PZT has high piezoelectric coupling coefficient and has low maximum operating temperature about 200˚C.However, PZT is dangerous because it contains 60% lead, which represents a possible ecological hazard, according to Malic et al., (2005).

Therefore, in recent years, lead-free piezoelectric materials have been gained much attention. According to Panda & Sahoo, (2015), barium titanate (BT) is the first lead-free piezoelectric materials discovered during the World War II. In 1952, PZT was discovered and it is has better piezoelectric properties due to the occurrence of morphotrophic phase boundary makes it is an excellent candidates than BT. Other than that, Smolenski et al., (1960) has reported the existence of bismuth sodium titanate (BNT) but the sintering temperature of BNT is high about 1200 ˚C. In consequences, due to the volatility of bismuth, the high sintering temperature will results the loss of bismuth in the composition. According to Panda, (2009) ,even though BNT is the best option to replace PZT due to its high Curie temperature about 320˚C, but still it cannot replace PZT because of it has high coercive field and high electrical conductivity.

Until then, Saito et al., (2004) had developed a textured potassium sodium niobate (KNN) based ceramics and the properties are quite comparable to the unmodified PZT. KNN has high electrical properties, high Curie temperature (T_c) about 420˚C and friendly environment material. The idea of switching of PZT to KNN is supported by the Waste Electrical and Electronic Equipment (WEEE)'s law in 2006 and the usage of certain Hazardous Substances in electrical and electronic equipment (RoHS) is restricted due to protect the health and environment, Li & Wang (2012).

The studies will be continuously conducted to find out the best output in the performance of KNN. In this study, the different annealing and pyrolysis temperature will be the variables on the enhancement of the structural and ferroelectric properties of KNN.

1.2 Problem Statement

In recent years, the studies on potassium sodium niobate (KNN) have been gained much attention by researchers. It is because KNN is friendly environment material if compared to lead zirconia titanate (PZT) which has a large amount of lead which is a toxic substance and can cause damage to the kidney, brain, and nervous system as well as affect the children's intelligence according to Du et al., (2006). Therefore, in electrical devices as well as the thin film application, the lead-free piezoelectric material such as KNN is the best choice to replace the PZT.

However, According to Haugen et al.,(2015), the fabrication of KNN by conventional solid state reaction technique is difficult due to the volatility of potassium (K) and sodium (Na) at higher calcination temperatures and duration which will results in the loss of potassium and sodium in the composition . In order to encounter the difficulties, according to Yan et al.,(2010) sol-gel method is introduced to synthesis KNN because of sol-gel method offers a low fabrication temperature.

In this study, KNN thin film is more preferable than KNN bulk ceramics. According to Yan et al.,(2010), memory, micro sensor and micro-actuator usually used ferroelectric and piezoelectric thin films compared to bulk ceramics. It is because, ferroelectric and piezoelectric thin films offer a lower operating voltage, easy to integrate with the Silicon (Si) technology and the cost is lower due to the less machining process according to Dausch et al., (2000).

To get the optimum properties of KNN thin film, KNN thin film need to undergo pyrolysis and annealed at certain temperatures.

1.3 Objective

The objectives of this project are:

i. To fabricate KNN thin film via sol-gel spin coating technique.
ii. To determine suitable pyrolysis and annealing temperature for fabrication of KNN thin film.
iii. To optimize the structural and ferroelectric properties of KNN thin film.

1.4 Scope

The scope of this study is to analyze the crystal structure, dielectric of KNN thin film by varying the pyrolysis and annealing temperature.

The fabrication of KNN thin film will be carried out by a sol-gel spin coating technique. The precursor of KNN will be prepared using the sol-gel route. Sodium acetate (CH_3COONa), potassium acetate (CH_3COOK), niobium penthaethoxide ($Nb(OC_2H_5)_5$), 2-metoxyethanol ($CH_3OCH_2CH_2OH$) and acetyl acetone will be used as the chemicals. Further, the sol of KNN will be deposited by on silicon substrate using spin coating method and will undergo pyrolysis and annealing process. The pyrolysis and the annealing temperature will be varied in the range of 250˚c until 350˚c for pyrolysis and 650˚c until 750 ˚c respectively. Common materials analysis such as XRD, SEM, and RAMAN spectroscopy and dielectric properties testing using LCR meter will be employed to study the effect of different pyrolysis and annealing temperature on the structure properties of KNN film. In addition, dielectric properties will be investigated to confirm the reliability of the film for further piezoelectric application.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of Piezoelectric

According to Cady et al., (1946), Nobel Laureates, Pierre and Jacques Curie were discovered the piezoelectricity when studying the effect of the pressure on the generation of electric charges by some natural crystals such as quartz, tourmaline, Rochelle salt and etc. Piezoelectric material is the material that can polarized spontaneously when the mechanical stress is applied and the material also can work in the reverse way. The word of "piezo" means pressure. This word is originated from the Greek word. Piezoelectricity also can be known as pressure electricity. In other words, the net electrical charge will appear when the crystal is under the pressure such as squeezing and stretching the crystals. Deformation of the crystal's shape resulting in the balancing of the positive and negative ions by pushing the atom closer together or further apart. There are several of piezoelectric materials that have been discovered such as barium titanate, lead zirconate titanate, potassium sodium niobate and etc. However, the most extensively used piezoelectric material is PZT. The behavior of the piezoelectric material makes the researchers are actively studied about it.

2.1.1 Piezoelectric ceramics

Piezoelectric ceramics are very hard, chemically inert and humidity or other atmospheric factor insensitive. Based on Kong and Wang (2003) ,the piezoelectric ceramic have the unstructured polarization. It is because the charge concentration of the unit cells are distinct from each other at a certain temperature range.

According to Yu (2014), Figure 2.1 (a) shows the crystal structure of the barium titanate above its Curie temperature. Its Curie temperature is about 120˚C. Above the Curie temperature, barium titanate appears to be in cubic crystal structure with Ba^{2+} ion at cube corner, O^{2-} ions at the face center and Ti^{4+} at the body center. Meanwhile, Figure 2.1 (b) shows the crystal structure of barium titanate below its curie temperature and it is slightly deformed with Ba^{2+} and Ti^{4+} ions displaced relative to O^{2-} ions. When it is slightly deformed, the material will exhibit the piezoelectric properties.

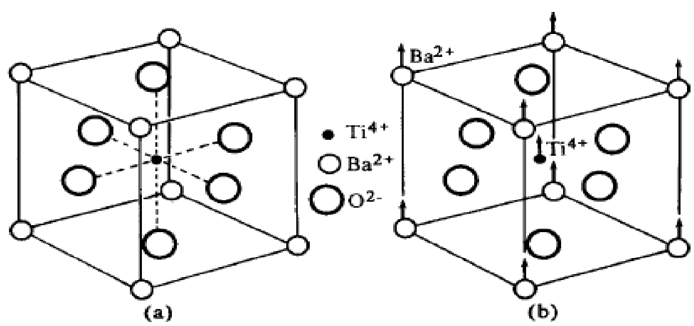

Figure 2.1 :(a) Crystal structure of barium titanate above Curie temperature, (b) Crystal structure of barium titanate below Curie temperature (Yu, 2014)

The most popular piezoelectric ceramics used is lead zirconate titanate (PZT). PZT has the perovskite structure with the general formula of ABO_3 same with the other piezoelectric materials. In perovskite structure, A sites is located at the corner of the cubes meanwhile B sites is located at the center of the body. The oxygen atom, O is bonded to the A and B sites and oxygen atom will be located at the face centered of the cubic structure. PZT is a solid solutions between lead zirconate ($PbZrO_3$) which is known as PZ and lead titanate ($PbTiO_3$) known as PT. According to,Panda & Sahoo,(2015), the rich compositions of zirconia (Zr) is in the rhombohedral state and the rich compositions of titanium (Ti) is in the tetragonal state and the morphotropic phase boundary of PZT is at the composition, x= 0.48 of $PbTiO_3$. The permittivity, piezoelectric coefficient and piezoelectric coupling coefficient is maximum at the MPB. Figure 2.2 shows the phase diagram of PZT (Panda & Sahoo 2015).

From Figure 2.2, the horizontal line is the boundary of the paralectric and ferroelectric state. The vertical line is the MPB at x = 0.48 of $PbTiO_3$ is separating the rhombohedral and tetragonal phase. There are 14 direction of the polarization which is 6 from the tetragonal and 8 from the rhombohedral and these polarization will be producing the high piezoelectric and dielectric properties.

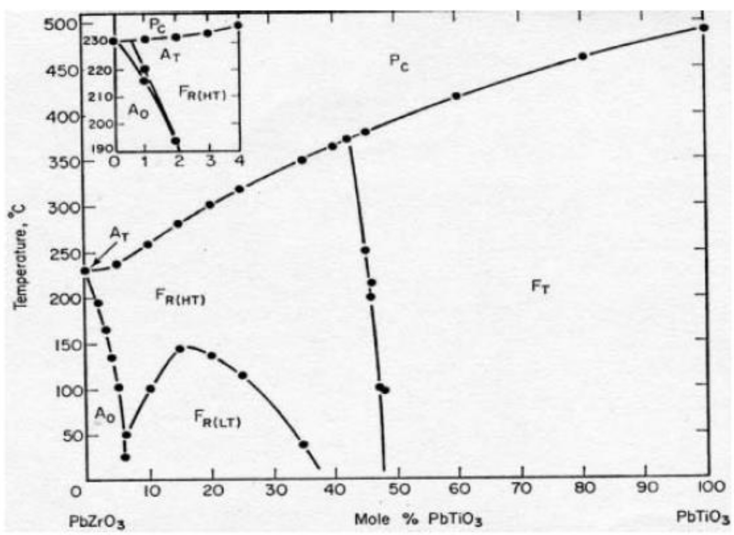

Figure 2.2: Phase diagram of PZT (Panda & Sahoo 2015)

However, the usage of PZT is dangerous as it is containing 60 % of lead (Pb) and can lead to the environmental pollution. Therefore, many of the research is conducted to find the alternatives to find the suitable material to switch the usage of PZT.

2.1.2 Lead free piezoelectric material

The most extensively used piezoelectric material is lead zirconate titanate (PZT) because of its high piezoelectric properties. However, due to the toxicity of the lead that may accumulates in the organism and causing to the brain damage and nervous system, PZT is forbidden to be used in many countries according to Hong et al., (2016). To solve the problem, many researchers studied the materials that can replace the PZT. There are several lead free piezoelectric materials that have been discovered to be used in the electronic industries. All the lead free piezoelectric materials have different piezoelectric properties.

There are two categories to classify the piezoelectric materials which are the piezoelectric ceramics with perovskite structure and non-perovskite structure. The piezoelectric materials that have perovskite structure is barium titanate (BT), bismuth sodium titanate (BNT) and potassium sodium niobate (KNN). For the non perovskite structure, the piezoelectric materials are bismuth layer structured ferroelectrics (BLSF) and tungsten bronze type ferroelectrics. However, the material that exhibit the good piezoelectric properties is the piezoelectric material with the perovskite structure (Panda & Sahoo 2015) .

Barium titanate (BT) is the first piezoelectric material that discovered during World War II. The piezoelectric coefficient of BT is high. According to Panda & Sahoo (2015), the piezoelectric coefficient of BT that is synthesized from the conventional solid state is 190 pC/N. However the Curie temperature for BT is relatively low (T_c = 120˚C) and it causes the usage of BT in the piezoelectric application is unsuitable as the working temperature range is limited.

Other than BT, Smolenski & Wang (1960) has reported the existence of bismuth sodium titanate (BNT). However, the sintering temperature for BNT is large that is 1200˚C. In consequences, due to the volatility of bismuth, the high sintering temperature will results the loss of bismuth in the composition. Compared to the other lead free piezoelectric materials, BNT has the high piezoelectric properties. According to Panda, (2009) ,even though BNT is the best option to replace PZT due to its high Curie temperature 320˚C , but still it cannot replace PZT because of it has high coercive field and high electrical conductivity and Takenaka & Nagata (2012), reported that the Curie temperature of BNT single crystal is about 340˚C and 540˚C.