SYNTHESIS AND CHARACTERIZATION OF $K_{0.5}Na_{0.5}NbO_3$ THIN FILM

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

by

NG SIEW XING
B051510270
950107-04-5188

FACULTY OF MANUFACTURING ENGINEERING
2019

DECLARATION

I hereby, declared this report entitled "Synthesis and Characterization of $K_{0.5}Na_{0.5}NbO_3$ Thin Film" is the results of my own research except as cited in reference.

Signature :……………………………………

Author's Name : NG SIEW XING

Date : 20th June 2019

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Hons.). The members of the supervisory committee are as follow:

……………………………………...

(Prof. Madya Dr. Mohd Warikh Bin Abd Rashid)

ABSTRAK

Tujuan kajian ini adalah untuk menghasilkan filem nipis Potassium Sodium Niobate (KNN) dan mengaji kesan suhu annealing yang berbeza atas morfologi dan resistiviti filem nipis. KNN filem nipis dibuat melalui kaedah sol-gel dengan campuran dua jenis prekursor alkali, iaitu potassium asetat (CH_3COOK), dan natrium asetat (CH_3COONa), niobium (V) etoksida ($C_{10}H_{25}NbO_5$), acetylacetone dan pelarut organik 2-Methoxyethanol. Seterusnya, larutan homogen yang dihasilkan akan didepositkan pada substrat silikon dengan pendekatan salutan spin. Filem-filem nipis akan menjalani 250℃ pirolisis selama 5 minit dan kemudian disedut pada suhu dari 600℃ hingga 650℃. Selepas itu, pelbagai analisis seperti X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) dan Raman Spectroscopy dijalankan untuk mengaji kesan pirolisis dan suhu penyepuhlindapan dijalankan untuk mendapati suhu annealing yang optimum. Selepas data dianalisis, kajian memdapati bahawa suhu annealing yang paling optimum untuk KNN filem adalah 650℃.

ABSTRACT

The aim of this study is to synthesis Potassium Sodium Niobate (KNN) thin film and evaluate the morphology and resistivity of the thin film which fabricated with various annealing temperatures. Firstly, KNN is produced by Sol-gel method where the two alkaline precursors, namely potassium acetate (CH_3COOK), and sodium acetate (CH_3COONa), niobium (V) ethoxide ($C_{10}H_{25}NbO_5$), acetylacetone and the organic solvent 2-Methoxyethanol are mixed. Next, the homogenous solution is then deposited on the silicon substrate with the aid of spin coating approach. The as-deposited thin films will undergo 250℃ pyrolysis of for 5 min and then being annealed at the ranged temperature which are from 600℃ to 650℃. Following this, a series of material analysis such as X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Raman Spectroscopy on the effects of pyrolysis and annealing temperature is carried out as to find out the optimum annealing temperature. Looking into the results, it was discovered that 650℃ is the optimum annealing temperature as it shows the best crystallization of KNN grain.

DEDICATION

I dedicate this research report affectionately to the following:

My beloved father, Ng Moo Ee

My appreciated mother, Chua Boon Neo

My adored six sisters

For giving me moral support, money, cooperation, encouragement and also understandings.

Thank You So Much & Love You All Forever

ACKNOWLEDGEMENT

In the name of God, the most gracious, the most merciful, with the highest praise to God that I manage to complete this final year project successfully without difficulty.

My respected supervisor, Prof. Madya Dr. Mohd Warikh Bin Abd Rashid for the great mentoring that was given to me throughout the project. Besides that, I would like to express my gratitude to the lab assistances and technicians, for their kind supervision, advice and guidance as well as exposing me with meaningful experiences throughout the study.

Last but not least, I would like to give a special thanks to my best friends who gave me much motivation and cooperation mentally in completing this report. They had given their critical suggestion and comments throughout my research. Thanks for the great friendship.

Finally, I would like to thank everybody who was important to this FYP report, as well as expressing my apology that I could not mention personally each one of you.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

LIST OF EQUATIONS

LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

PZT	- Lead Zirconia Titanate
$PbZrO_3$	- Lead Zirconate
$PbTiO_3$	- Lead Titanate
$^{\circ}C$	- 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
$C_{10}H_{25}NbO_5$	- Niobium penthaethoxide
$CH_3OCH_2CH_2OH$	- 2-Metoxyethanol
$K_{0.5}Na_{0.5}NbO_3$	- Potassium Sodium Niobate
XRD	- X-ray diffraction
SEM	- Scanning electron microscopy
BLSF	- Bismuth layer structured ferroelectrics
pC/N	- Pico per newton

Na	- Sodium
K	- Potassium
PLD	- Pulsed laser deposition
ALD	- Atomic layer deposition
CVD	- Chemical vapor deposition
μm	- micrometer
rpm	- revolution per minute
cm	- centimetre
g/mol	- gram per mol
g	- gram
N_2	- Nitrogen
Nm	- Nanometer
μA	- microampere

CHAPTER 1

INTRODUCTION

This chapter is intended to provide background information of the product. It covers background of product, problem statement, objectives, scope and organisation.

1.0 Background of Study

Ferroelectric material is the one that exhibit polarization spontaneously under its transition temperature known as the Curie temperature. Ferroelectric material is commonly use in the electrical filed as its instinctive polarization can be reconstructed by utilization of any electrical sources for any designated purposes. Out of the 250 ferroelectric materials, Lead Zirconate Titanate (PZT) is the most popular due to it superb pyroelectric properties ($x < 0.3$) and had been chosen for the production of first generation of pyroelectric thin-film sensors from the start until now (Said et al., 2017). Valasek, (1921) had mentioned that a solid solution of ferroelectric $PbTiO_3$ and anti-ferroelectric $PbZrO_3$ can form PZT that widely used in various sensor, actuator, and transducer applications.

In the new market research report "Piezoelectric Devices Market by Material, Product, Application - Global Forecast to 2022", the market of piezoelectric devices is expected to have continuously growth till the year of 2020 with a growing rate of Compound Annual Growth Rate (CAGR) of 4.88 %. With that also predicted the need on PZT will increase proportionally too (Markets and Markets Research, 2009-2018). However, this incremental of demand is not ideal because the emission of toxic substances such as Lead Oxide (PbO) will increase relatively along their life cycle. The PbO emission is harmful to living organism and atmosphere. Recently, the presence of >60 wt% lead oxide (PbO) in PZT-based piezoelectric ceramics had raised the awareness related to environmental and health matter (Ibn-Mohammed et al., 2018). Consequently, the motivation to investigate and develop the lead-free piezoelectric compositions has been triggered due to the strictly environmental regulations that are being enforced globally (Seog et al., 2018).

As mentioned by Li et al. (2012) and Castañeda-Guzmán et al. (2017), Potassium Sodium Niobate $(K_xNa_{1-x})NbO_3$(KNN) thin film has been one the most widely investigated materials among the variety types of lead-free perovskites over the last decade. The first studies of the $KNbO_3$-$NaNbO_3$ pseudobinary phase equilibria were reported in the late 1960s and early 1970s (Koruza et al., 2018). Then in the following about half decades time, KNN thin film with x= 0.5 (Egerton and Dillon et. al., 1957) had been proved in the past researches as one of the potential material that can replace the PZT due to their indistinguishable characteristics of ferroelectric and piezoelectric when compare to PZT. KNN had been proved on its higher piezoelectric properties, such as higher piezoelectric constant (~300 pC/N), higher remanent polarization (14 μC/cm2), higher dielectric constant (~700), lower coercive field (~140 kV/cm) and relatively higher Curie temperature (420℃) in previous researches (Akmal et al., 2018).

All the mentioned characteristic can be vary by manipulating some of the parameters along the synthesis process of KNN. This study is about to discover the alternation of parameters in producing KNN which will boost the material output performance.

1.1 Problem Statement

Despite of the advantages and flexibility of PZT as material in making electrical components, the lead waste produced during manufacturing and recycling would cause serious hazard to humans and the environment. Hence, the ideal of switching the 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 (Wang & Li, 2012).

KNN can be produce in term of bulk or in thin film. Todays, the concern of thin film is high due to the increase of consciousness on energy preservation, miniaturization and integrating (Wiegand et al., 2013). There are extensive of researches to study the properties of KNN thin film making through various fabrication methods or parameters. For example, pulsed laser deposition (PLD) (Bäuerle et al., 1999), sputtering (Berg et al., 1988), and Sol–Gel process (Wiegand et al., 2013). Sol–Gel process is relatively cost saving alternative because it is not vacuum-based, low manufacturing temperature, controllable component composition, and low equipment cost when compared to the other (Yan et al., 2010).

Among the rational of Sol-Gel process gained more preference, the temperature played significant roles. The annealing or sintering temperature had big range of difference in the past researches. Yan et al., (2010) studied rapid thermal annealing at 500–650 ℃ for 5 min and showed that KNN with sintering temperature 650 ℃ had the best crystallization of grain. On the other hand, Li et al., (2012) claimed that the best annealing temperature for KNN thin film is 600 ℃ with respect to the range of 450 ℃ to 700 ℃ for 5 min. Anyhow, inadequate study shows the optimum temperature among 600 ℃ to 650 ℃.

One of the way to optimise the properties of KNN thin film, the fabrication parameters variances mentioned above must be eliminated and explore any relationship of these parameters could related to its properties and resistivity.

1.2 Objectives

The objectives of this study are:

a) To fabricate the KNN thin film via sol-gel spin coating technique.

b) To determine the optimum annealing temperature of KNN thin film.

c) To analysis the structural properties and resistivity of the KNN thin film.

1.3 Scope

This study will focus on the analysis of morphology structure, crystallographic properties and resistivity of KNN which made by sol-gel spin coating technique.

The raw chemical for sol gel made KNN are the two alkaline precursors, namely potassium acetate (CH_3COOK), and sodium acetate (CH_3COONa), niobium (V) ethoxide ($C_{10}H_{25}NbO_5$), acetylacetone and the organic solvent 2-Methoxyethanol. Next, the homogenous solution of these chemical mixture is then deposited on the silicon substrate with the aid of spin coating approach. Further, the as-deposited thin films will undergo 250 ℃ pyrolysis of for 1 min. Besides, annealing process will be manipulated within the ranged temperature which are from 600 ℃ to 650 ℃. Following this, a series of material analysis on the consequences of pyrolysis and annealing temperature is carried out using few characterization machine, such as X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Raman Spectroscopy outcome of compositional on the resistivity properties is subsequently examine with LCR meter.

1.4 Significant of study

There are some potential benefits that can be gained by the community after the completion of this study. There will be more preferable and uniform parameters in fabricating the low cost KNN thin film via sol-gel method and the properties performances of KNN thin film might be amplified.

1.5 Organization of the Report

This project focuses on the synthesis and characterization of the KNN thin film via sol-gel. First, an introduction to the problem is given. Next, a thorough analysis of a variety parameters of fabrication with related to the properties of KNN are discussed based on the sufficient literature reviews had been made. Then, a proper and standard design of experiment will be set on the methodology chapter. A series of analysis will be carried out which based on the result gained through the experiment. Finally, conclusion is made.

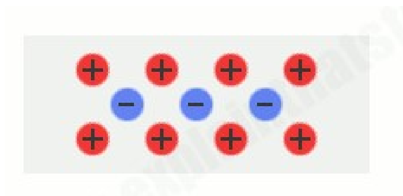
CHAPTER 2

LITERATURE REVIEW

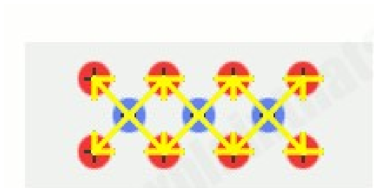
2.1 Introduction to Piezoelectric

According to Sunar, (2018), "Piezoelectricity" can be related to mechanical and electric fields which means the mechanical input such as strain will be resulted as an electric output like potential. The coupling as mentioned is known as direct piezoelectricity, where normally utilised in piezoelectric sensors and transducers. In contrast, the coupling acts in the vice versa is called converse piezoelectricity. Back off to the past, the Curie brothers were first discovered this direct piezoelectric effect in single crystal quartz by 1880 (Jalili, 2010). The research had found that quartz generated electrical charge or voltage when exerted with pressure (Uchino, 2010). Then one year after 1880, the converse piezoelectric effect had successfully determined by Gabriel Lippmann in 1881 and plentiful of series study had been carried out based on this material and consequently applied as actuators in control science and technologies (Sunar, 2018).

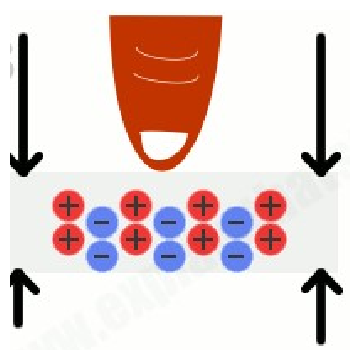
Piezoelectric material have this special characteristic due to the atoms inside the piezoelectric crystals. Although the atoms are unsymmetrically arranged, but they are electrically neutral as positive charge in one place cancels out a negative charge nearby. However, if it being exerted on external stimulation such as squeeze or stretch, the charge neutralization being destroy and causing net electrical charges to appear. There are several type piezoelectric materials that have been disclosed such as barium titanate, lead zicronate titanate, potassium sodium niobate and etc. Nonetheless, the most broadly used is PZT, therefore more research will be studied regarding PZT material. The working principle of piezoelectric material is illustrated in Figure 2.1 (a-d). Initially, the charges in a piezoelectric crystal are exactly balanced. The effects of the charges exactly cancel out, leaving no net charge on the crystal faces. If you squeeze the crystal (massively exaggerated in this picture), you force the charges out of balance. The effects of the charges (their dipole moments) no longer cancel one another out and net positive and negative charges appear on opposite crystal faces, thus the material had become charge unbalanced, exhibits potential difference.



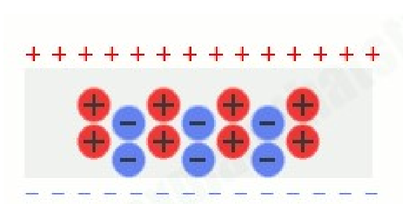
(a) Entire charges balanced.



(b) The effects of the charges exactly cancel out, no net charge.



(c) Force the charges out of balance when squeezed.



(d) Net positive and negative charges appear on opposite crystal faces.

Figure 2.1 The working principle of piezoelectric material (Chris Woodford, 2018)

2.1.1 Piezoelectric Ceramics

Piezoelectric ceramics exhibit mechanical strength, resistive to chemical and less sensitive to humidity. According to Kong & Wang, (2003), the piezoelectric ceramics have differences charge concentration between unit cells at specific temperature range and lead to disorganized polarization.

Yu *et al.,* (2014) had stated in his study as what Figure 2.2 (a) displays about the barium titanate's crystal structure when it is beyond the Curie temperature, about 120◦C. Barium titanate presented to be in cubic crystal structure with the Ba^{2+} ion at cube corner O^{2-} ions at the face center and the Ti^{4+} at the body center when achieve more than 120◦C. Meantime, the crystal structure has illustrated in Figure 2.2 (b). The barium titanate deformed more or less with Ba^{2+} and Ti^{4+} ions displaced relative to O^{2-} ions. Thereupon, the material will show the piezoelectric properties.

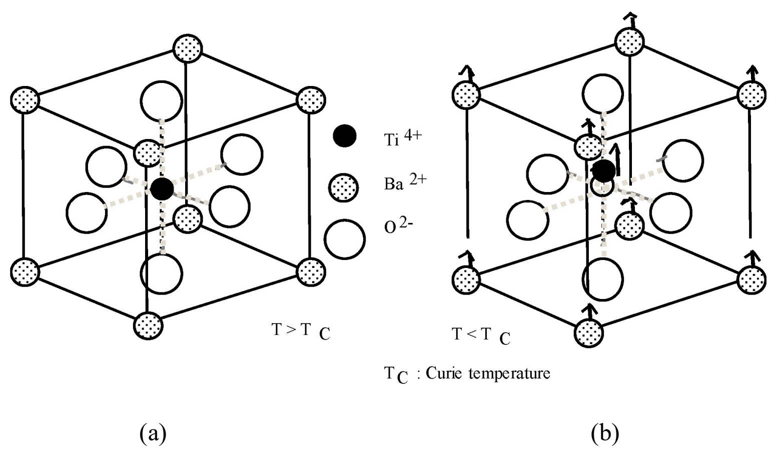


Figure 2.2 (a) Crystal structure of barium titanate above Curie temperature, (b) Crystal structure of barium titanate below Curie temperature (Huber, 2005)

The most favour choice of piezoelectric ceramics in industry is lead zicronate titanate (PZT). PZT owned the perovskite structure with general formula of ABO_3 same as 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. Both A and B sites are linked by an oxygen atom, O at the face centered of the structure. PZT is a solid solutions which combined lead zicronate ($PbZrO_3$), PZ and lead titanate ($PbTiO_3$), PT. Panda & Sahoo (2015) has