UNIVERSITI TEKNIKAL MALAYSIA MELAKA

EFFECT OF ZnO NANOWHISKERS ON THE $K_{0.5}Na_{0.5}NbO_3$ THIN FILM VIA THE HYBRID SOL GEL ROUTE

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

By

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APPROVAL

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

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ABSTRACT

The aim of this study is to analyze the effect of adding zinc oxide nano whiskers (ZnO) on potassium sodium niobate (KNN) thin film. The study was initially about piezoelectric ceramics which seems to be gaining interest among manufacturers recently. However, the main material used commonly for this component is lead zirconate titanate (PZT) and it contains toxic substances that would be harmful to both environment and health. Hence, this study suggested that KNN is one of the most suitable candidates to replace PZT. Firstly, the precursors solution for KNN must be prepared and there will be a total of three different KNN solution which is of different ZnO powder concentration, 0.1%, 0.3% and 0.5%. The solution is then used to coat and pyrolysis repeatedly until optimize number of coating layers achieved. Then, it undergoes annealing with optimized temperature. The sample went through X-ray Diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and four-point probe analysis. Both XRD and Raman spectroscopy are used to identify the molecule and compositional of KNN sample. SEM showed cuboid-like structure as referred in other studies and four-point probe proved that the resistivity changes in every concentration. The analysis was made to relate all the results with each other. In conclusion, it is found that 0.3% concentration of KNN is the best optimum concentration for ZnO to be added.

ABSTRAK

Tujuan kajian ini adalah untuk menganalisis kesan penambahan zink oksida nano (ZnO) di filem kalium natrium niobate (KNN). Kajian ini pada mulanya mengenai seramik piezoelektrik yang semakin mendapat minat di kalangan pengeluar. Walau bagaimanapun, bahan utama yang digunakan biasanya untuk komponen ini adalah zirkonat titanat plumbum (PZT) dan ia mengandungi bahan-bahan toksik yang akan menjadi berbahaya kepada alam sekitar dan kesihatan. Oleh itu, kajian ini mencadangkan bahawa KNN adalah di kalangan calon-calon yang sesuai untuk menggantikan PZT. Pertama, prekursor untuk KNN mesti disediakan dan akan ada sejumlah tiga cecair dengan kepekatan yang berbeza KNN yang yang berbeza kepekatan serbuk ZnO, 0.1%, 0.3% dan 0.5%. yang kemudiannya digunakan untuk kot dan pirolisis berulang kali sehingga jumlah optimum lapisan salutan dicapai. Kemudian, ia menjalani penyepuhlindapan dengan suhu yang dioptimumkan. sampel telah melalui X-ray Diffraction (XRD), spektroskopi Raman, mikroskop elektron pengimbas (SEM) dan analisis telah dilakukan. Kedua-dua XRD dan spektroskopi Raman digunakan untuk mengenal pasti molekul dan komposisi KNN. SEM menunjukkan struktur KNN seperti dalam kajian lain dan empat mata analisa membuktikan bahawa perubahan kerintangan dalam setiap jumlah zink oksida nano yang ditambah. Analisis itu dibuat untuk membandingkan keputusan dengan satu sama lain. Kesimpulannya, didapati bahawa 0.3% kepekatan KNN adalah kepekatan optimum terbaik ZnO yang perlu ditambah.

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In the name of ALLAH, the most gracious, the most merciful, with the highest praise to Allah that I manage to complete the final project successfully in within the given time. My respected supervisor, Associate Professor Dr Mohd Warikh Bin Abd Rashid who had guide me throughout all the way along the journey with much dedication. Besides, I would like to express my gratitude towards all the lecturers that helped me directly and indirectly during the process. A big thank you for all the technicians in the laboratory that constantly helped during the preparation and analysing of sample.

Last but not least, a special thanks to my friends and course mates for the motivation mentally and physically while going through difficulties during the process of completing the study. They had given me suggestions of solutions and useful opinions throughout the journey.

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LIST OF ABBREVIATIONS

BLSF	-	Bismuth Layer-Structured Ferroelectrics
CSD	-	Chemical Solution Deposition
FESEM	-	Field Emission Electron Microscopy
MPB	-	Morphotropic Phase Boundary
PIC700	-	PI Ceramic GmbH
RoHS	-	Restriction of Hazardous Substances
SEM	-	Scanning Electron Microscopy
WEEE	-	Waste Electrical and Electronic Equipment
XRD	-	X-ray Diffraction

LIST OF SYMBOLS

% wt	-	Weight percentage
$(NaBi(TiO_3)_2)$	-	Bismuth titanate
$(Nb_2OC_2H_5)_5$	-	Niobium ethoxide
°C	-	Degree Celsius
µm	-	Micrometre
Ar^+	-	Argon ion
$BaTiO_3$	-	Barium titanate
$C_3H_8O_2$	-	2-Methyoxyethanol
CeO_2	-	Cerium (IV) oxide
CH_3COOK	-	Potassium acetate
CH_3COONa	-	Sodium acetate
CuO	-	Copper (II) Oxide
I	-	Applied current
K	-	Potassium
K_2CO_3	-	Potassium carbonate
kHz	-	Kilo Hertz
KNN	-	Potassium Sodium Niobate
ln	-	Natural logarithm

MnO	-	Manganese (II) Oxide
Na_2CO_3	-	Sodium carbonate
Nb_2O_5	-	Niobium oxide
SnO_2	-	Tin (IV) Oxide
t	-	Film thickness
Ta	-	Tantalum
V	-	Voltage drop
V_2O_5	-	Vanadium Oxide
WO_3	-	Tungsten trioxide
Zn^{2+}	-	Zinc ion
ZnO	-	Zinc Oxide

CHAPTER 1

INTRODUCTION

1.1 Background

Due to rapid revolution in the industry and high demand of micro-components such as sensors, actuators and transducers, the development of piezoelectric ceramics increases tremendously (Moulson & Herbert., 2003). Lead zirconate titanate (PZT) is one of the most widely used piezoelectric ceramic material. Based on the article by Yamamoto et al., (1996), PZT have morphotropic phase boundary (MPB) which made it possess superior electrometrical properties, excellent ferroelectric and piezoelectric properties. However, recent studies on lead-free piezoelectric compositions became a priority since PZT composed of 60 % and above weight toxic lead which would affect human health and lead to various environmental issues. One of the famous alternative material for lead-free piezoelectric is potassium sodium niobate (KNN).

The state of KNN focused in this project is the KNN thin film. Hence, potassium sodium niobate, $K_{0.5}Na_{0.5}NbO_3$ (KNN) thin film will be prepared using sol-gel synthesis. The thin film will be formed from two mixture of precursors which is a mixture of potassium acetate and sodium acetate, and mixture of niobium (V) ethoxide and 2-methyoxyethanol. The perovskite KNN is known for its superior ferroelectric and piezoelectric properties as it has polymorphic phase boundary. On the other hand, these properties are very much poorer in pure KNN compared to PZT. It is a challenge to obtain a dense KNN material due to the volatility of potassium and sodium at elevated temperature. Therefore, modification and improvement of KNN are continuously been studied to produce high-quality KNN thin-films as an effort to create a lead-free piezoelectric material. To enhance the sinterability properties of KNN, various sintering agents' oxide could be used such as copper oxide (CuO), cerium (IV) oxide (CeO_2), and tungsten trioxide (WO_3).

This project focuses on studying the effect of modifying KNN thin film with zinc oxide (ZnO) nano whiskers. Previously, ZnO are to be known to be used on KNN as an attempt to decrease the dielectric losses of the material compared to other compound such as copper (II) oxide (CuO) or manganese (II) oxide (MnO). Hence, it is believed that ZnO is capable of improving the piezoelectric properties and the weakness of KNN which is easily evaporated at high temperature.

1.2 Problem Statement

Based on article, the use of hazardous substances such as lead in piezoelectric is restricted by European Union. Lead zirconate titanate (PZT) are made up of more than 60 % wt. of lead oxide (PbO) and according to past researches, lead (Pb) is a heavy toxic metal that is urged to be eliminated from all electric and electronic devices. Waste Electrical and Electronic Equipment (WEEE) and Restriction of Hazardous Substances (RoHS) enforce that recycling or reusing electric and electronic component must completely be forbidden as it provokes human health and environment safety (EU-Directive 2002/96/EC, 2003). The maximum concentrations of lead allowed was only 0.1 % which made PZT out of the list. However, PZT is still used until today as there are no material that could perform better or at the same level as PZT as a piezoelectric device. Therefore, endless effort on producing alternative lead-free material are being developed every day and it is constantly improving. Although there is no alternative material found are yet to be in the same level and exhibit the perfect criteria needed to replace lead zirconate titanate (PZT), there are few possible candidates of material to replace it. For example, $BaTiO_3$, $Bi_{0.5}Na_{0.5}TiO_3$-based perovskites, bismuth layer-structured ferroelectrics (BLSF), and $(K,Na)NbO_3$ (KNN)-based perovskites (Wang & Jing-Feng,2012). In this study, potassium sodium niobate (KNN) shows high potential of being a candidate to replace PZT. Based on report made by Saito et al. (2004), modified KNN with lithium (Li), tantalum (Ta) and antimony (Sb) are able to reach piezoelectric constant higher than a basic soft PZT could do. Researchers believe that modified KNN has the potential to able to mimics morphotropic phase boundary (MPB) composition of PZT. MPB is a composition phase where PZT displays its ultimate ultrahigh piezoelectric response. Hence, if modified-KNN can imitate PZT structural composition, the usage of lead-based piezoelectric are able to completely be eliminated. However, KNN-based system is much more complicated than it seems. Despite having high piezoelectric constant, the dielectric and piezoelectric properties in pure KNN is quite low compared to PZT. KNN tend to have issues on sintering process and it is volatile at high temperature which makes it difficult to obtain a dense KNN ceramics. Thus, this will lead to poor piezoelectric properties. The main concern is that potassium (K) and sodium (Na) is highly volatile with high sintering temperature, it has small sintering windows and possibilities of secondary phases evolution. Several solutions have been studied to improve this condition. For example, by using different advanced process hot pressing and spark plasma sintering. These techniques are effective to reach high densities and better properties compared to conventional method but somehow it requires cautious investigation and the most effective parameters to produce high quality result of KNN. Furthermore, these methods are very costly compared to conventional sintering process and it is unsuitable for mass production with varies of shape for piezoelectric. Another solution is that by adding compounds with low melting temperature such as copper oxide (CuO), magnesium oxide (MnO) and vanadium oxide (V_2O_5) as sintering aid. Ramajo et al., (2014b), mentioned that by adding these compounds oxygen vacancies will be produced in the perovskite lattice which will then harden the ferroelectric properties of the material. Hence in this study, it is decided that Zinc Oxide (ZnO) is embedded to KNN for modifications. It is believed that by doping KNN with ZnO will initiate structural and microstructural evolution of the final output.

Previously, most findings tend to focus on improving the properties of KNN which originates from bulk ceramic structure. Generally, KNN in bulk state is thicker compared to thin film and this would then limit its application in micro-electro-mechanical system devices (MEMS). Bulk ceramics too require bonding agent to attach it to certain devices in MEMS which is non-economical and complex to be done. Therefore, one of the best ways to prevent any complexity during the process is to reduce the size as in thin film state instead. Thin film thickness is commonly less than 1 μm and has high demand for research purposes. However, there were still concerns on producing high quality and consistent thin films. Hence, the synthesis and characterization of KNN thin films which will be done using sol gel method will be studied carefully in order to obtain good thin films.

1.3 Objectives

The objectives of this study are:

i. To fabricate ZnO-doped KNN thin film through sol-gel method by varying the concentration of ZnO as 0.1, 0.3 and 0.5 mol%.
ii. To analyze the structural and electrical properties of ZnO-doped KNN thin film
iii. To optimize the concentration of ZnO concentration of the doped KNN thin film.

1.4 Scope

The study is systematically to investigate the effect of doping nano whiskers zinc oxide (ZnO) on potassium sodium niobate (KNN) thin film. The purpose is to create an improved alternative lead-free piezoelectric material physically and chemically. The fabrication of ZnO-doped KNN thin films will be fabricated using chemical solution deposition (CSD) process technique. The parameters used for basic steps are optimized parameters based on the fabrication of pure KNN thin films such as annealing temperature of 650 °C and five number of coating layers. The optimized parameters are made constant so that the parameter for ZnO can be investigated. Therefore, there will be three different concentration of ZnO which is 0.1, 0.3, and 0.5 mol%. This is to compare and study the best optimized concentration of ZnO to be applied in fabricating KNN thin films.

Once fabrication of ZnO-doped KNN thin film is successful, it will then be characterized to study its structure and properties. The analysis of crystallographic properties and molecular vibration of the doped thin film will be studies using X-ray diffraction (XRD), Raman spectroscopy and field emission electron microscopy (FESEM). This is to study any changes in the structural and phases when the ZnO concentration varies. Besides, the electrical properties of the thin film will be studied too since the main function of piezoelectric is highly related to its electrical properties' performance. The electrical properties investigated will be its dielectric and piezoelectric properties. It will be studied through impendence analyzer and four-point resistivity measurement.

1.5 Significant of Study

The main purpose of this study is to help improve and modify lead zirconate titanate (PZT) material to be lead-free. For example, potassium sodium niobate (KNN) are used as the alternative KNN in this study to avoid the usage of lead or any harmful compounds. This is a huge effort on reducing toxicity and restricting hazardous substances in technology development. This is significant to protect our environment and future generations as most of the substances use to develop latest technology contains harmful substances. The study on effect of ZnO nano whiskers when added to KNN are equally important too. It is to widen and enhance the usage of ZnO as a compound that would help improve properties of other compounds which would contribute to produce improved and better materials in the future industry.

1.6 Organization of report

The report consists of five chapters which are introduction, literature review, methodology, results and discussion and lastly conclusion and proposal to further the study. Introduction briefly explains overall view about KNN as an alternative for lead-free piezoelectric material, modification of KNN with zinc oxide and the importance of lead-free materials.

Then, literature review will consist of review from journals, articles or books on KNN and modified KNN with zinc oxide. This chapter will explain on past studies and the attempts made on these materials to create a lead-free piezoelectric material. This chapter also introduces varies of compounds and materials used to create lead-free material. These chapter will somehow guide and provide more understanding about this project.

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significant of the methods used will be briefed too. In methodology, the three-category analysis will be explained which is in term of physical, mechanical and electrical. All the results will be shown in the next chapter, result and discussion. This chapter analyses and describe the results obtained. Finally, conclusion wraps up the whole project by stating facts obtained from the analyzed results.

1.7 Summary

Introduction basically introduces about the study that will be made and the content of it. Firstly, background generally brief the history of piezoelectric, material used, and relation with the study. It also tells about the alternative material used, potassium sodium niobate (KNN) and oxide used which is zinc oxide (ZnO). The purpose of using the alternative material and doping it with a sintering agent was explained briefly too. Next, the general problem for this study is clarified in problem statement which summarized the major purpose of doing the study. There are three main objectives in this study. Objectives are one of the important elements in this chapter which represents the direction of this study and its main goal. Then, the area of working, methods planned to be used, tests planned to be done are briefly explained in scope. Scope helps to summarize the plan on analyzing the compounds produced in this study. As mentioned, the analysis will be based on the physical, mechanical and electrical properties of the compound. Besides, this chapter highlights the importance of carrying out this study although similar study has been made before. Finally, this chapter briefly outline the organization of the whole report.