UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Faculty of Manufacturing Engineering

LEAD-FREE PIEZOELECTRIC ENERGY HARVESTER BASED ON OPTIMISED POTASSIUM SODIUM NIOBATE THIN FILM

Maziati Akmal binti Mat Harttar @ Mohd Hatta

Doctor of Philosophy

2017

LEAD-FREE PIEZOELECTRIC ENERGY HARVESTER BASED ON OPTIMISED POTASSIUM SODIUM NIOBATE THIN FILM

MAZIATI AKMAL BINTI MAT HARTTAR @ MOHD HATTA

A thesis submitted
in fulfillment of the requirements for the degree of Doctor of Philosophy

Faculty of Manufacturing Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2017

DECLARATION

I declare that this thesis entitled "Lead-free piezoelectric energy harvester based on optimised potassium sodium niobate thin film" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ....

Name :

Date :

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Doctor of Philosophy.

Signature	:	…………………………………...
Supervisor Name	:	
Date	:	

DEDICATION

To my beloved mother and father,

my husband and my son...

This humble work is dedicated for all of you who taught me to be patience in completing my work, who never fail to give continous support, du’as and encouragement during difficult time of this journey.

ABSTRACT

Piezoelectric energy harvester (PEH) is considered as a robust power source, which can power the electronic devices by scavenging small magnitudes of energy from ambient vibration. The fundamental advantage of PEH lies on the inherent ability of the piezoelectric material to generate electricity depending on the amount of vibration applied on the material. Although lead zirconate titanate (PZT) is the most common type of piezoelectric material used, the toxicity of PZT content has damaged the environment and health, in which it necessitates the discovery of lead-free piezoelectric material. Hence, potassium sodium niobate (KNN) is chosen as the potential candidate since good piezoelectric properties can be achieved by compositionally-engineered the perovskite structure. However, the thermal treatment of KNN at high temperature is challenging due to alkali metal cations volatility. In order to address this issue, a series of systematic reviews and a consecutive study on KNN energy harvester was conducted. In the present study, KNN thin films were fabricated via chemical solution deposition method. The effects of the annealing temperature and various number of coating layers on both the structural and electrical properties were looked into in order to find the optimum annealing temperature and coating layers to fabricate KNN thin films. The present study has shown that KNN thin film annealed at 650 °C presented a well-crystallised orthorhombic perovskite structure without the presence of secondary phase which confirmed by X-ray powder diffraction analysis. Crystallinity, molecular vibration, surface morphology, and resistivity were found to depend on the coating layers. Particularly, the optimum properties were found for KNN thin films with five coating layers. In addition, the structural and electrical properties were strongly affected by yttrium doping. All the thin films had a preferred (0 0 1) orientation with formation of pure orthorhombic perovskite structure. Small shift on Raman active mode, together with dense and homogenous surface morphology were obtained for 0.5 mol% yttrium-doped KNN. Besides, 0.5 mol% yttrium-doped KNN had intermediate electrical resistivity (2.153×10^6 Ω.cm), low dielectric loss (0.018 %), high dielectric permittivity (508), and high quality factor (25.730). Next, finite element modelling was performed to determine the resonance frequency of the as-fabricated KNN thin film to generate the optimum voltage and power output. The performance of KNN energy harvester was compared with a commercial lead based material, namely PZT-5H. Both harvesters showed a comparable output power of 0.104 mW and 0.115 mW for KNN and PZT-5H, respectively. Further, energy harvester performance analysis involving finite element modelling and experimental testing recorded a maximum voltage of 0.968 V and a power output of 0.1067 mW, when 0.5 mol% yttrium-doped KNN was resonated at 2098.7 Hz. To compare with pure KNN, 0.5 mol% yttrium-doped KNN exhibited a relatively desirable electromechanical coupling factor about 0.49, which has the potential as an energy harvester to substitute PZT in the future.

ABSTRAK

Penuai tenaga piezoelektrik (PEH) dianggap sebagai sumber kuasa mantap, yang dapat memberi kuasa kepada peranti elektronik dengan cara memerangkap magnitud kecil tenaga daripada getaran ambien. Kelebihan asas PEH terletak pada keupayaan yang ada pada bahan piezoelektrik untuk menjana tenaga elektrik bergantung kepada jumlah getaran yang dikenakan kepada bahan. Walaupun plumbum titanat zirkonat (PZT) adalah bahan piezoelektrik yang paling biasa digunakan, ketoksikan kandungan PZT telah merosakkan alam sekitar dan kesihatan, menyebabkan perlunya penemuan bahan piezoelektrik bebas plumbum. Oleh itu, kalium natrium niobat (KNN) dipilih sebagai pilihan berpotensi kerana sifat-sifat piezoelektrik yang baik dapat dicapai melalui pengubahsuaian komposisi struktur perovskit. Walau bagaimanapun, rawatan haba KNN pada suhu tinggi adalah mencabar kerana kemeruapan logam alkali kation. Untuk menangani isu ini, siri tinjauan sistematik dan kajian berturut-turut terhadap penuai tenaga KNN dilakukan. Dalam kajian ini, filem nipis KNN direka melalui kaedah pemendapan larutan kimia.. Kesan suhu penyepuhlindapan dan pelbagai bilangan lapisan salutan pada kedua-dua sifat-sifat struktur dan elektrik dikaji untuk mencari suhu optimum penyepuhlindapan dan lapisan lapisan untuk menghasilkan filem nipis KNN. Menurut analisis yang dijalankan, filem nipis KNN disepuh lindap pada 650 ℃ mempunyai struktur perovskit ortorombik yang dibentuk tanpa kehadiran fasa sekunder setelah dibuktikan dengan analisa pembelauan X-ray. Penghabluran, getaran molekul, morfologi permukaan, dan kerintangan didapati bergantung kepada setiap bilangan lapisan salutan. Terutamanya, sifat-sifat optimum ditemui dalam filem nipis KNN dengan lima lapisan salutan. Di samping itu, sifat-sifat struktur dan elektrik amat dipengaruhi oleh pendopan yttrium. Semua filem-filem nipis mempunyai orientasi pilihan (0 0 1) dengan pembentukan struktur perovskit ortorombik tulen. Perubahan kecil pada mod aktif Raman, beserta morfologi permukaan yang homogen dan padat telah diperoleh untuk 0.5 mol% yttrium-didopkan KNN. Di samping itu, 0.5 mol% yttrium-didopkan KNN mempunyai kerintangan elektrik yang sederhana (2.153×10^6 Ω.cm), kehilangan dielektrik yang rendah (0.018 %), ketelusan dielektrik yang tinggi (508), dan faktor kualiti tinggi (25.730). Seterusnya, pemodelan unsur terhingga dijalankan untuk menentukan frekuensi resonans filem KNN sebagaimana yang telah difabrikasi, untuk menjana output kuasa dan voltan optimum. Prestasi penuai tenaga KNN dibandingkan dengan bahan berasaskan plumbum komersial, iaitu PZT-5H. Kedua-dua penuai menunjukkan kuasa output yang setanding iaitu 0.104 mW dan 0.115 mW bagi KNN dan PZT-5H. Seterusnya, analisis prestasi penuai tenaga melibatkan pemodelan unsur terhingga dan pengujian eksperimen merekodkan voltan maksimum sebanyak 0.968 V dan output kuasa 0.1067 mW, apabila 0.5 mol% yttrium-didopkan KNN bergema pada 2098.7 Hz. Untuk membandingkan dengan KNN tulen, 0.5 mol% yttrium-didopkan KNN menunjukkan faktor gandingan elektromekanik yang diingini bernilai 0.49, yang berpotensi sebagai penuai tenaga untuk menggantikan PZT pada masa hadapan.

ACKNOWLEDGEMENTS

First, I credit none more than my principal supervisor, Associate Professor Dr. Mohd Warikh for his continuous support, advice and feedbacks for the completion of this work. His guidance has been truly priceless to me. I would also like to thank my co-supervisor, Dr. Umar Al-Amani for his thoughtfulness and knowledge. Not to forget Dr. Muhammad Zaimi for his constructive feedbacks and valuable comments on any possible improvements of my study.

Special thanks also go to the MIMOS FA lab members for sharing their knowledge about atomic force microscopy, transmission electron microscopy and focused ion beam analysis. In addition, I am thankful to Mrs. Faezahana from Microelectronic and Nanotechnology-Shamsudin Research Centre of UTHM for her direction in X-ray diffraction study. My appreciation also goes to Dr. Aliza Aini from IIUM for her training and assistance in developing electrical measurement and finite element modelling. To all the technical staffs at Faculty of Manufacturing of UTeM, the skills and knowledge they possessed had helped me a lot.

I wish to express my gratitude to all my friends, in particular Sis Noraini, Hanisah, Nurul, Amira, Madihah, Azuwa, Suraya Laily, Nur Aidawaty and Chiew Tsung Heng for their kind cooperation and inspiration. Above all, I wish to thank my parents, Mrs. Robitoh and Mr. Mohd Hatta for their unconditional love and endless support during my difficult time. You two are the best! I deeply thankful to my husband (Muhammad Alif) and my son (Muhammad Haziq) for not complaining me when I was not around and letting me your shoulder to cry on all these years. I knew I had spent a lot of time on this work. Without all of you, this thesis would never have been possible. Last but not least, the financial supports by Ministry of Higher Education Malaysia and International Islamic University Malaysia are gratefully acknowledged.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

AFM	-	Atomic force microscopy
DTA	-	Differential thermal analysis
EDX	-	Energy dispersive X-ray spectroscopy
FEM	-	Finite element modelling
FESEM	-	Field emission scanning electron microscopy
FWHM	-	Full width half maximum
GOF	-	Goodness-of-fit
HRTEM	-	High resolution transmission electron microscopy
IEEE	-	Institute of Electrical and Electronics Engineering
JCPDS	-	Joint committee on powder diffraction standards
K	-	Potassium
KNN	-	Potassium sodium niobate
Na	-	Sodium
Nb	-	Niobium
PZT	-	Lead zirconate titanate
PEH	-	Piezoelectric energy harvester
TGA	-	Thermogravimetric analysis
XRD	-	X-ray diffraction
Y	-	Yttrium

LIST OF SYMBOLS

A	-	Acceleration magnitude
C	-	Damping constant
D	-	Charge displacement
d	-	Piezoelectric coefficient
E	-	Electric field
E_p	-	Young Modulus of piezoelectric material
E_s	-	Young modulus of substrate
ε_{r}	-	Permittivity
ε_{o}	-	Permittivity in free space
f_a	-	Anti-resonance frequency
f_r	-	Resonance frequency
k	-	Electromechanical coupling factor
L	-	Inductance
M	-	Seismic mass
P	-	Power output
R	-	Resistance
R_{wp}	-	Weighted profile R-factor
R_{exp}	-	Expected R-factor
S	-	Strain
T	-	Stress

t_p	-	Thickness of piezoelectric layer
t_s	-	Thickness of substrate
$tan\ \delta$	-	Dielectric loss
Q	-	Quality factor
V	-	Voltage output
ω	-	Excitation frequency
w_p	-	Width of piezoelectric material
w_s	-	Width of substrate
χ^2	-	Goodness of fit
z_p	-	Neutral axis of piezoelectric layer
z_s	-	Neutral axis of substrate
ξ	-	Dimensionless damping ratio

LIST OF PUBLICATIONS

Journals

1. **Maziati Akmal**, **M.H**., Warikh, A.R.M., Azlan, U.A.A., Azam, M.A., and Ismail, S., 2016. Effect of Amphoteric Dopant on the Dielectric and Structural Properties of Yttrium Doped Potassium Sodium Niobate Thin Film. *Materials Letters*, 170, pp. 10–14. *ISI Indexed*
2. **Akmal, M.H.M.**, Warikh, A.R.M., Azlan, U.A.A., Azam, M.A., Anand, T.J.S., and Moriga, T., 2016. Structural Evolution and Dopant Occupancy Preference of Yttrium-Doped Potassium Sodium Niobate Thin Films. *Journal of Electroceramics*, pp. 1–8. *ISI Indexed*
3. **Maziati Akmal**, **M.H**., Warikh, M., Rashid, A., Azlan, U.A.H., Azmi, A., Azam, M.A., Moriga, T., 2016. Influence of Yttrium Dopant on the Structure and Electrical Conductivity of Potassium Sodium Niobate Thin Films. *Materials Research*, 19, pp. 1–6. *ISI Indexed*
4. **Maziati Akmal**, **M.H.**, Azlan, U.A., Mohd Warikh, A.R., and Nurul Azuwa, A., 2015. Enhanced Structural and Electrical Properties of Lead-freeY-Doped (K, Na) NbO_3 Thin Films. *Jurnal Teknologi*, 21, pp. 67–71. *Scopus Indexed*
5. **Maziati Akmal**, **M.H.**, Warikh, M., Rashid, A.B.D., Al, U., and Azlan, A., 2015. Rare-Earth Doped Potassium Sodium Niobate (KNN): A Review. Ceramics-Silikaty, 59(2), pp. 158–163. *ISI Indexed*