UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Faculty of Electronic and Computer Engineering

FABRICATION OF LEAD FREE PIEZOELECTRIC CERAMICS FOR ENERGY HARVESTING APPLICATIONS

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A thesis submitted
in fulfillment of requirements for the degree of Master of Science
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DECLARATION

I declare that this thesis entitled "Fabrication of Lead Free Piezoelectric Ceramics for Energy Harvesting Applications" 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.

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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 Master of Science in Electronic Engineering.

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

DEDICATION

To my beloved family

ABSTRACT

Energy harvesting is a process by collecting a small amount of energy from the ambient environment. In this research, the concept of energy harvesting system was implemented using thick film piezoelectric ceramics transforming mechanical vibration energy into electrical energy. In line with the growing awareness of the environmental hazards with the present of lead, this thesis proposed two types of lead free ceramic material: barium titanate ($BaTiO_3$) and potassium sodium niobate (KNN). The major challenges for energy harvesting from a lead free piezoelectric device are that the electrical output power is relatively small compared to the minimum requirement of electrical power for operating small electronic devices. The main objective of the project is to fabricate thick film lead free piezoelectric ceramic which able to produce high output power for the application of energy harvesting. In order to fabricate lead free thick film piezoelectric ceramics, thick film technology is selected due to its simplicity and low cost compared to thin film technology. One of the performance indicators for a piezoelectric energy harvesting material is the measurement of the piezoelectric charge coefficient, d_{33}. Two of the materials, $BaTiO_3$ and KNN were characterized and studied to compare its performance. The fabrication process involves the development of lead free piezoelectric paste, thick film screen printing and electrical polarization. The lead free piezoelectric paste was developed by mixing a composition of functional element and permanent binder in the powder form and pine oil as the temporary binder to make the paste printable. The lead free piezoelectric ceramic was fabricated by screen printing a few layers of piezoelectric film, which stack on top of an electrode layer on a substrate and finished with another layer of electrodes on the top of the sandwiched structure of electrode-piezoelectric-electrode. The polarization was performed by applying high DC electric fields at ranges of up to 2 kV at an elevated temperature of around 250 °C using hotplate. The performance of each of the lead free thick film piezoelectric ceramic was evaluated based on its charge coefficients, voltages output, and power output. The parameters of the film were varied with different screen printing process, co-firing duration and controlled temperature rate to determine the optimum lead-free piezoelectric ceramics. The result shows that the piezoelectric charge coefficient of KNN is 38 *p*C/N for a thickness of 140 μm which is able to generate a maximum power of 12.25 nW at external resistive load of 25 kΩ which is better performed compared to $BaTiO_3$ with d_{33} of 25 *p*C/N and maximum output power of 0.423 nW for the similar thickness and external resistive load. In conclusion from this experimental result, it shows that KNN thick film performs better compared to $BaTiO_3$ thick film as an energy harvesting material.

ABSTRAK

Penuaian tenaga adalah satu proses mengumpul sejumlah tenaga yang kecil daripada suasana persekitaran. Dalam kajian ini, konsep sistem penuaian tenaga telah dilaksanakan menggunakan filem tebal piezoelektrik seramik mengubah dengan tenaga getaran mekanikal kepada tenaga elektrik. Selaras dengan kesedaran yang semakin meningkat tentang bahaya alam sekitar dengan plumbum masa kini, tesis ini telah mencadangkan dua jenis bahan seramik bebas plumbum: barium titanat ($BaTiO_3$) dan kalium natrium niobat (KNN). Cabaran utama bagi menghasilkan tenaga dari peranti piezoelektrik bebas plumbum adalah keluaran kuasa elektrik adalah agak kecil berbanding keperluan minimum kuasa elektrik untuk peranti elektronik kecil beroperasi. Objektif utama projek ini adalah untuk menghasilkan filem tebal piezoelektrik seramik bebas plumbum yang mampu menghasilkan keluaran kuasa yang lebih tinggi untuk aplikasi penuaian tenaga. Dalam usaha untuk menghasilkan filem tebal piezoelektrik seramik bebas plumbum, teknologi filem tebal dipilih kerana kesederhanaan dan kos rendah berbanding dengan teknologi filem nipis. Salah satu petunjuk prestasi untuk bahan penuaian tenaga yang piezoelektrik adalah ukuran pekali piezoelektrik, d_{33}. Dua daripada bahan-bahan, $BaTiO_3$ dan KNN telah dikaji untuk membandingkan prestasinya. Proses fabrikasi telah melibatkan penghasilan pes piezoelektrik bebas plumbum, percetakan skrin filem tebal dan polarisasi elektrik. Pes piezoelektrik bebas plumbum telah dibangunkan dengan mencampurkan komposisi unsur berfungsi dan pengikat kekal dalam bentuk serbuk dan minyak pinus sebagai pengikat sementara untuk membuat pes boleh dicetak. Piezoelektrik seramik bebas plumbum telah difabrikasikan dengan percetakan skrin beberapa lapisan filem piezoelektrik, yang disusun di atas satu lapisan elektrod pada substrat dan ditambah dengan satu lagi lapisan elektrod pada bahagian atas struktur yang diapit elektrod-piezoelektrik-elektrod. Polarisasi telah dilakukan dengan menggenakan medan elektrik DC tinggi pada jarak sehingga 2 kV pada suhu ditinggikan sekitar 250 darjah celsius menggunakan plat panas. Prestasi setiap filem tebal piezoelektrik seramik bebas plumbum dinilai berdasarkan pekali casnya, keluaran voltan, dan keluaran kuasa. Parameter filem itu telah diubah dengan proses percetakan skrin yang berbeza, tempoh pembakaran dan kadar suhu terkawal untuk menentukan piezoelektrik seramik bebas plumbum yang optimum. Hasil kajian menunjukkan bahawa pekali caj piezoelektrik KNN adalah 38 pC/N untuk ketebalan 140 µm yang mampu menjana kuasa maksimum pada 12.25 nW dengan beban rintangan luaran 25 kΩ mencatatkan prestasi yang lebih baik berbanding $BaTiO_3$ dengan d_{33} pada 25 pC/N dan keluaran kuasa maksimum pada 0.423 nW untuk ketebalan dan beban rintangan luaran yang sama. Kesimpulan, hasil eksperimen ini, menunjukkan bahawa filem tebal KNN adalah lebih baik berbanding filem tebal $BaTiO_3$ sebagai bahan penuaian tenaga.

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LIST OF ABBREVIATIONS

Abbreviations

AC	-	Alternating Current
AlN	-	Aluminum Nitride
BT	-	$BaTiO_3$, Barium Titanate
BNT	-	Bismuth Sodium Titanate
BST	-	Barium Strontium Titanate
DC	-	Direct Current
EH	-	Energy Harvesting
EU	-	European Union
KNN	-	$(K,Na)NbO_3$, Potassium Sodium Niobate
LTCC	-	Low Temperature Co-fired Ceramics
NBBT	-	$(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$ (NBBT)
NKBT	-	Sodium Potassium Bismuth Titanate
Pb	-	Lead
PVDF	-	poly(vinylidene fluoride)
PZT	-	$Pb(Zr_xTi_{1-x})O_3$, Lead Zicronate Titanate
RF	-	Radio Frequency
SEM	-	Scanning Electron Microscope

Parameters (physical)

d	-	piezoelectric constant
d_{33}	-	piezoelectric charge coefficient on z-direction
d_{31}	-	piezoelectric charge coefficient on x-direction
E	-	electric field
ε_r	-	relative dielectric permittivity
f	-	frequency
f_r	-	resonant frequency (piezoelectric)
F	-	applied force
g	-	g-level, gravitational level
h	-	height
l	-	length
Ω	-	ohm
n	-	nano
μ	-	mirco
t	-	thickness
T	-	temperature
T_c	-	Curie temperature
$V_{o/c}$	-	open-circuit voltage output
V_{out}	-	voltage output
w	-	width
W	-	Watt

LIST OF APPENDICES

LIST OF PUBLICATIONS

The research papers produced and published during the course of this research are as follows:

JOURNALS

Muhamad Haffiz Mohd Radzi and Kok Swee Leong, 2016. "**Fabrication of $BaTiO_3$ thick-film lead-free piezoelectric ceramic by using screen printing method**". *ARPN Journal of Engineering and Applied Sciences*, vol. 11(14), pp.8787-8793.

CONFERENCE PROCEEDING

Muhamad Haffiz Mohd Radzi and Kok Swee Leong, 2015. "**Investigation of the piezoelectric charge coefficient d_{33} of thick-film piezoelectric ceramics by varying poling and repoling conditions**", In: AIP Conf. Proc., *International Conference on Mathematics, Engineering and Industrial Applications 2014 (ICOMEIA 2014),* Penang, Malaysia, vol. 1660, pp 070083.

CHAPTER 1

INTRODUCTION

This short introductory chapter defines the research background and describes the motivation for carrying out the research, problem statement, specifies the research objectives, and scope of research. The descriptions of the research contributions will also be briefly mentioned. The chapter ends by presenting an organization of the thesis structure.

1.1 Terminology

Energy harvesting is the process by collecting the small amount of energy from exist ambient environment sources such as wind, flowing water, waste thermal, vibration, electromagnetic waves and solar (K.-I. Park *et al.*, 2010). The term “energy” is referred as an environmental energy that convert existing ambient sources such as vibrational energy as well as mechanical and thermal energy into electrical energy (Bowen *et al.*, 2014). Figure 1.1 depicted overview of energy harvesting technology from human activity or the ambient environment.

1.2 Research Background

There are many interesting applications of lead free piezoelectric devices towards energy harvesting for carrying out chemical analysis, biological analysis, mechanical analysis and electrical analysis (Smith *et al.*, 2008). However, the developments of the thick film lead free piezoelectric ceramics are still in early stage to explore the feasibility for electrical analysis (Cui *et al.*, 2012).

The evolution of scavenging energy from piezoelectric ceramics have a long history of being widely used in sensors and actuators (Li *et al.*, 2014). The thesis addresses the issues related with energy harvesting approaches which primarily utilizes lead free piezoelectric schemes based on the mechanical configuration for electrical determination.

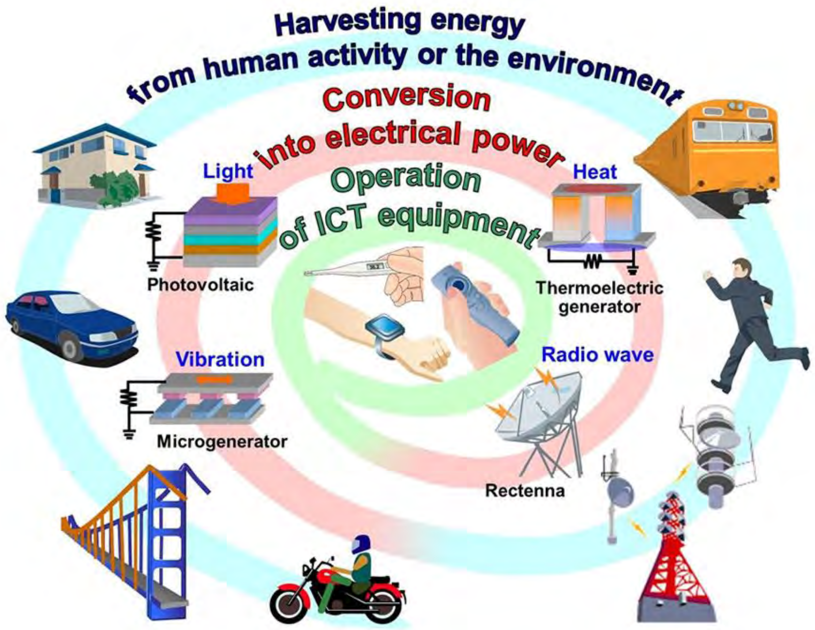

Figure 1.1 : Overview of energy harvesting (Adapted from Fujitsu Lab. Ltd. 2010).

Lead zirconate titanate (PZT) piezoelectric ceramics are commonly used in various electronics applications because of its superior performance piezoelectric properties. However, due to environmental and health concerns over high content of lead, lead free piezoelectric ceramics become the most encouraging candidates (Farooq and Fisher, 2014; Li *et al.*, 2014; Yin *et al.*, 2015). The lead free piezoelectric material is a potential replacement for the high performance lead-based material. Replacing currently used lead-rich materials with the new lead free material to avoid toxicity, whilst maintaining the necessary functionality, has become an urgent issue in the piezoelectric research field (Lee *et al.*, 2013). However, a high production cost and low reproducibility have limited a wide penetration to the market for this lead free material (Hansen, Astafiev and Zawada, 2009).