Enhanced Dielectric and Piezoelectric Properties of $Ba_{0.8}Sr_{0.2}Ti_{1-x}Sn_xO_3$ for Energy Harvester Applications

by

Nur Nadia Nasika Binti Mahamad Nasir
(2030313173)

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LIST OF ABBREVIATIONS

$BaTiO_3$	Barium Titanate
BST	Barium Strontium Titanate
BSTS	Barium Strontium Titanate Stannate
EDX	Energy Dispersive X-ray
MPB	Morphotropic Phase Boundary
PZT	Lead Zirconate Titanate
SEM	Scanning Electron Microscopy
XRD	X-ray Diffraction
MLCC	Multi Layered Ceramics Capacitors
$BaCO_3$	Barium Carbonate
$SrCO_3$	Strontium Carbonate
TiO_2	Titanium Oxide
SnO_2	Stannum Oxide
BPT	Barium Lead Titanate
$PbNb_2O_6$	Lead Meta Niobate
PT	Lead Titanate
BNT	Bismuth Sodium Titanate
$BiTiO_3$	Bismuth Titanate
RoHS	Restriction of Hazardous Substances
Pt	Platinum
SiC	Silicon carbide
DC	Direct current
ICDD	Inorganic Crystallography Diffraction Database
PDF	Powder Diffraction Files
FOM	Figures of merits

LIST OF SYMBOLS

d_{33}	Piezoelectric constant
g_{33}	Piezoelectric voltage constant
f	Frequency
A	Electrode area
C	Capacitance
d	Interplanar spacing
R	Resistance
S	Strain
T_c	Curie Temperature
t	Tolerance factor
$\varepsilon_\circ$	Dielectric constant in vacuum
ε_r	Relative dielectric constant
σ	conductivity
θ	Diffraction angle
λ	Wavelength of X-rays
ρ	Resistivity
ω	Angular frequency
tan δ	Dielectric loss
D	Charge displacement
T	applied stress
T_{cw}	Curie-Weiss constant
ΔT	Deviation from the Curie-Weiss law
r_A	Ionic radii of A-site cation
r_B	Ionic radii of B-site cation
r_O	Ionic radii of oxygen anion
E_a	Activation energy
eV	Electron volt
F	Farad
°C	Degree celcius
P	Power output
Q	Charge
Z’	Impedance
l	Thickness of the sample

Sifat Dielektrik dan Piezoelektrik yang Dipertingkatkan $Ba_{0.8}Sr_{0.2}Ti_{1-x}Sn_xO_3$ untuk Aplikasi Penuaian Tenaga

ABSTRAK

Piezoelektrik telah membantu meningkatkan kehidupan seharian kita dengan menghasilkan banyak aplikasi berguna seperti suntikan bahan api automotif, akselerometer, transformer dan motor piezoelektrik, kawalan getaran, sistem penentududukan mikro, pengesan ultrabunyi, penjana, pencetak inkjet, dan penuai tenaga. Penuai tenaga digunakan untuk menukar daya menjadi tenaga elektrik. Bahan piezoelektrik mendapat perhatian paling banyak berbanding kaedah lain kerana bahan itu sendiri secara langsung dapat menukar tenaga regangan yang diterapkan menjadi tenaga elektrik. Walau bagaimanapun, bahan piezoelektrik yang paling praktikal yang terdapat di pasaran ialah Plumbum Zirkonat Titanat (PZT) yang mengandungi sejumlah besar Plumbum (Pb) yang memberi implikasi buruk kepada alam sekitar. Keadaan ini memaksa penemuan bahan piezoelektrik bebas plumbum dalam beberapa tahun ini. Seramik berasaskan Barium Titanat ($BaTiO_3$) telah menjadi calon yang menjanjikan sifat yang mungkin setanding dengan Pb apabila didopkan dengan unsur lain. Dalam kajian ini, $Ba_{0.8}Sr_{0.2}Ti_{1-x}Sn_xO_3$ (di mana x = 0, 0.02, 0.04, 0.06, 0.08 dan 0.10 telah disediakan melalui kaedah tindak balas keadaan pepejal konvensional. Sampel dicirikan menggunakan Pembelauan Sinar-X (XRD), Penganalisis Spektroskopi Impedansi, Penganalisis Uji Piezoelektrik dan Mikroskopi Elektron Pengimbasan (SEM). Analisis XRD menunjukkan, $Ba_{0.8}Sr_{0.2}Ti_{1-x}Sn_xO_3$ mempunyai peralihan fasa struktur dari tetragonal ke kubik apabila kandungan Sn meningkat. Analisis dielektrik, $Ba_{0.8}Sr_{0.2}Ti_{1-x}Sn_xO_3$ menunjukkan suhu Curie, T_c beralih ke arah suhu yang lebih rendah dari 65 °C hingga 5 °C disebabkan oleh penggantian Sn^{4+} dengan radius ion yang lebih besar daripada Ti^{4+} di bahagian B. Komposisi pada x = 0 mempunyai pemalar dielektrik tertinggi disebabkan oleh momen dipol spontan yang banyak. Walau bagaimanapun, penggantian Sn dengan x = 0.02 menunjukkan sedikit penurunan pada pemalar dielektrik. Bagi sampel dengan x = 0.04, pemalar dielektrik telah menunjukkan terdapat dua peralihan fasa pada 40° C (fasa tetragonal - kubik) dan fasa lain yang berdekatan dengan ~ 25 ° C yang merupakan fasa ortorhombik - teragonal (T_{O-T}). Kewujudan fasa orthorhombik - teragonal (T_{O-T}) telah meningkatkan pemalar dielektrik. Pada x = 0.06 dan 0.08, menunjukkan penurunan berterusan dielektrik dengan peningkatan kandungan Sn disebabkan oleh perubahan struktur kepada struktur kubik. Walau bagaimanapun, pemalar dielektrik sampel dengan x = 0.10 meningkat secara drastik kerana kesan mencubit di mana fasa rhombohedral - orthorhombik (T_{R-O}) dan fasa orthorhombic - tetragonal (T_{O-T}) bergabung, membentuk satu puncak yang luas di T_c. Pengukuran piezoelektrik menunjukkan sampel dengan struktur tetragonal, x = 0, mempunyai nilai d_{33} yang tinggi sebanyak 95 pC/N, nilai g_{33} sebanyak 8.66×10^{-3} Vm/N dan mempunyai kuasa keluaran, P yang tinggi sebanyak 0.8227 pm^3/J pada suhu bilik, yang sesuai untuk aplikasi penuai tenaga piezoelektrik. Apabila, Sn didopkan dengan $Ba_{0.8}Sr_{0.2}TiO_3$, nilai tertinggi bagi pemalar piezoelektrik d_{33} adalah sebanyak 61 pC/N, nilai g_{33} sebanyak 3.77×10^{-3} Vm/N dan mempunyai kuasa keluaran, P yang tinggi sebanyak 0.2300 pm^3/J direkodkan pada x = 0.02.

Enhanced Dielectric and Piezoelectric Properties of $Ba_{0.8}Sr_{0.2}Ti_{1-x}Sn_xO_3$ for Energy Harvester Application

ABSTRACT

Piezoelectricity improved our daily life by producing many useful applications such as automotive fuel injection, accelerometers, piezoelectric transformers and motors, vibration control, micro-positioning systems, ultrasonic sensor, generators, inkjet printers, and energy harvester. The energy harvester is used to convert force into electrical energy. Piezoelectric material becomes the most attention than other material because the material itself can directly convert applied strain energy into electrical energy. However, the most practical piezoelectric material available in the market is Lead Zirconate Titanate (PZT) which contained a large amount of Lead (Pb) that gives severe implications to the environment. This situation has forced the finding of lead-free piezoelectric material in recent years. Barium Titanate ($BaTiO_3$)-based ceramic has become the promising candidate that could have comparable properties to Pb when doped with other elements. In this study, $Ba_{0.8}Sr_{0.2}Ti_{1-x}Sn_xO_3$ where x = 0, 0.02, 0.04, 0.06, 0.08 and 0.10 were prepared using conventional solid-state reaction method. The samples were characterised using X-ray Diffraction (XRD), Impedance Spectroscopy analyser, Piezoelectric Test analyser, and Scanning Electron Microscopy (SEM). The XRD analysis shows that $Ba_{0.8}Sr_{0.2}Ti_{1-x}Sn_xO_3$ had a structural phase transition from tetragonal to cubic when Sn content increased. The dielectric analysis of, $Ba_{0.8}Sr_{0.2}Ti_{1-x}Sn_xO_3$ shows the Curie temperature, T_c shifted towards lower temperature from 65 °C to 5 °C was due to the replacement of Sn^{4+} with larger ionic radii than Ti^{4+} at B-sites. The composition with x = 0 has the highest dielectric constant because of large spontaneous dipole moments. However, the substitution of Sn with x = 0.02 shows a bit decrease in dielectric constant. For x = 0.04, the dielectric constant has revealed two-phase transition at 40 °C (tetragonal – cubic phases) and another phase near ~ 25 °C, which belongs to orthorhombic – tetragonal phases (T_{O-T}). The existence of orthorhombic – tetragonal phases (T_{O-T}) has increased the dielectric constant. At x = 0.06 and 0.08, the dielectric constant decreases by increasing the Sn contents due to the structural changes to the cubic structure. However, the dielectric constant of the sample with x = 0.10 drastically increased due to the pinching effect where rhombohedral – orthorhombic (T_{R-O}) phases and orthorhombic – tetragonal (T_{O-T}) phases merged, forming one broad peak at T_c. The piezoelectric measurement shows that a sample with a tetragonal structure, x = 0, has a high d_{33} value about 95 pC/N, g_{33} value about 8.66×10^{-3} Vm/N has the high output power, P about 0.8227 pm^3/J at room temperature, which is good for piezoelectric energy harvester application. When, Sn is doped in $Ba_{0.8}Sr_{0.2}TiO_3$, the highest value of the piezoelectric constant d_{33} is 61 pC/N, the value of g_{33} is 3.77×10^{-3} Vm/N and has a high output power, P of 0.2300 pm^3/J is recorded at x = 0.02.

CHAPTER 1 : INTRODUCTION

1.1 Research Background

Piezoelectric ceramic material is known to exhibit a unique effect called direct effect and converse effect. The direct effect is the capability of the material to change mechanical stress into electrical charge. In contrast, the converse effect is the ability of the material to produce mechanical force when an electric current is applied. These dual effects enable piezoelectric material to be used in various applications such as automotive fuel injection, accelerometers, piezoelectric transformers and motors, vibration control, micro-positioning systems, ultrasonic sensors and generators, inkjet printers, and energy harvester. Recently, the piezoelectric energy harvester has turn out to be the best energy harvester transducer options in the electronic industry. The usage of piezoelectric material for energy harvester has been utilized by California state for piezoelectric energy harvester application, where piezoelectric ceramics are scattered half-mile of highway in aiming to power 5000 homes in future (California Piezoelectric Highway, 2017). In order to understand the piezoelectric, the figure of merits for piezoelectric parameters such as the piezoelectric pressure coefficient (*d*ij), the piezoelectric voltage constant (*g*ij), power (P), and its temperature dependences is crucial to be understood.

The researchers have investigated several research areas to enhance the performance of energy harvester applications. Cain and Mitcheson have carried out some related project work about energy harvester application. Their work is associated with the energy roadmap, as demonstrated in Figure 1.1(Cain & Mitcheson, 2012). Based on Figure 1.1, each research area has its targets, assurance of deliverables, technologies, and enabling in science that was predicted to be achieved by a particular year. From 2014

until mid-2015, work on an intelligent adaptive system was performed and followed with nanoscale devices until mid-2016. After that, the enhancement of energy harvester application continued in the development of hybrid devices. However, as 2018 progresses and several years ahead, the most exciting research field for researchers will be device integration and the production of new materials. As a result, the aim of this research is to discover and develop new piezoelectric materials for energy harvester applications.

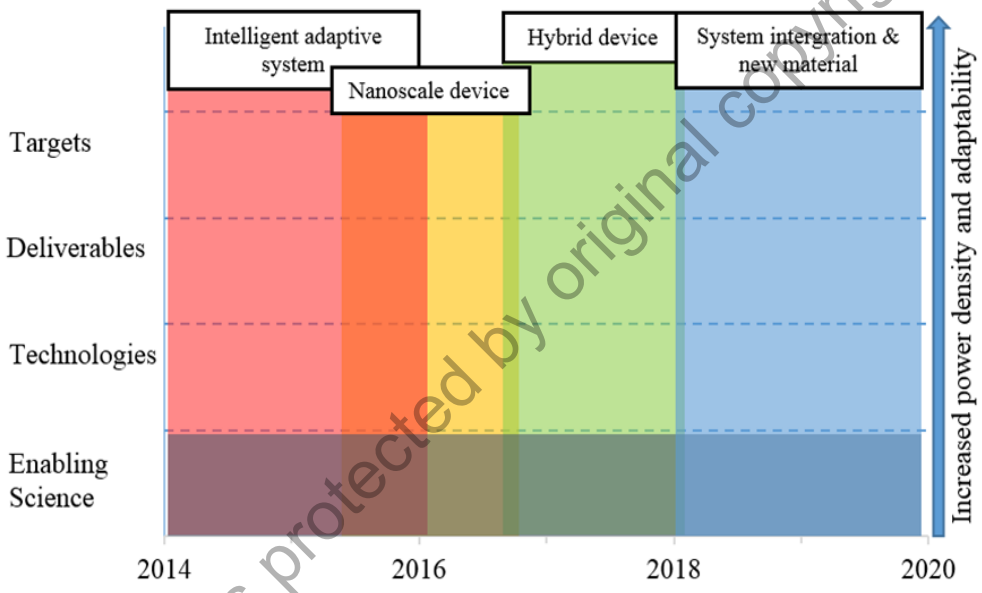

Figure 1.1 Roadmap of energy harvesting (Cain & Mitcheson, 2012)

1.2 Mechanism of piezoelectric materials

Piezoelectric material is classified by the dielectric materials that belongs in the class of non-centrosymmetric crystals structure. Even though the piezoelectric crystal is not symmetrically arranged but their electrical charges are perfectly balanced due to piezoelectric materials having random direction of dipoles in unit cells. However, the electric dipoles in the crystal become oriented during the polarisation process. This

process helps the direct piezoelectric effect happen where the electrical energy was generated when the mechanical stress is applied. Therefore, the oriented electric dipoles creates positive and negative charges on opposite sides, resulting in an electric field across the crystal (Vijaya, 2017).

In another way, when the external electric field is applied to the materials, symmetric displacements of anions and cations occur, resulting in significant net crystal deformation. The resultant strain is directly proportional to the applied electric field. The strain in a piezoelectric material is expansive or compressive, depending on the polarity of the applied field. This effect is known as the converse or indirect piezoelectric effect. Figure 1.2 shows the type of piezoelectric effect (Vijaya, 2017).

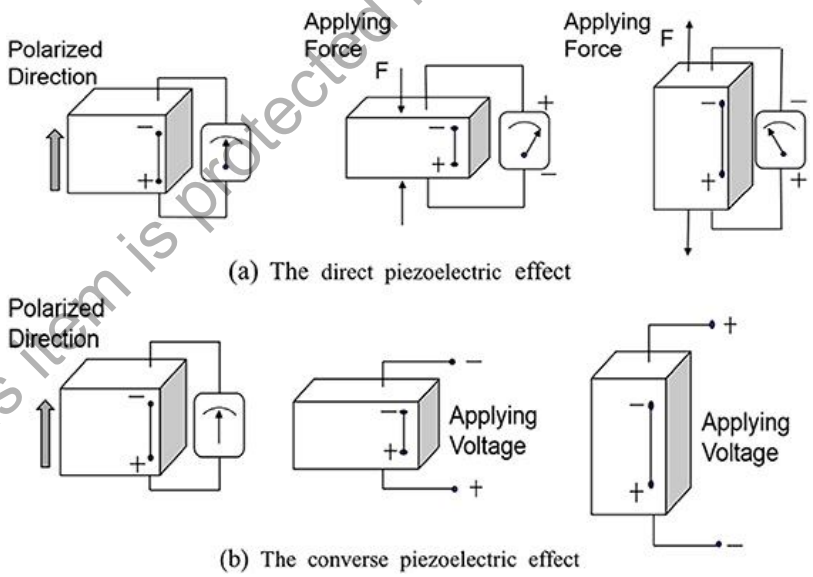

Figure 1.2 The piezoelectric effect (Shao, Hao and Wang, Hongxia and Fang, 2019)

1.3 Problem statement

To date, the most used material for the piezoelectric application is Lead Zirconate Titanate (PZT). It is because PZT exhibit high piezoelectric constant (375 pC/N) and high mechanical coupling coefficient, exhibit high curie temperature (T_c) in the range of 300 to 400 ºC, can be easily poled, has a wide range of dielectric constant, relatively easy to sinter at lower temperatures, and form solid solution compositions with variety of constituents, thus enabling a wide range of available properties (Bobic et al., 2018). Presently PZT-based piezoelectric ceramics are leading materials for piezoelectric transducers because of their impressive piezoelectric properties. However, more recently, there is now an increase in concern about the toxicity of lead-containing devices from the restriction of hazardous substances directive regulations (Leontsev & Eitel, 2010). Therefore, in 2015, the used of lead in electronic devices was completely restricted by The RoHS (Fasquelle et al., 2015)(Zheng et al., 2018). In order to resolve this problem, future research will be focused on the replacement of Pb-based material. Therefore, lead-free perovskite materials have widely investigated recently.

Barium titanate-based material is a promising candidate for lead-free piezoelectric material in piezoelectric material research with nearly PZT characteristics. Barium Titanate has piqued people's attention for more than 60 years because of its appealing properties such as chemically and mechanically very stable, it has ferroelectric properties at room temperature and above and also it is simple to make and use in the form of polycrystalline ceramics (Vijatović et al., 2008a). Because of its high dielectric constant and low loss characterisation, barium titanate ($BaTiO_3$) is used in capacitors and multilayer capacitors (MLCs) (Vijatović et al., 2008b). However, the piezoelectric constant for $BaTiO_3$ is about 191 pC/N, which is lower than PZT. Since then, further

investigations on the enhancement of pure $BaTiO_3$ by doping with other materials like strontium (Sr) and stannum (Sn) have been among the most intriguing for investigators from time to time.

1.4 Objectives

1. To synthesis the barium strontium titanate stannate (BSTS) with formula $Ba_{0.8}Sr_{0.2}Ti_{1-x}Sn_xO_3$ ($0 \leq x \leq 0.10$) by using conventional solid-state reaction method.

2. To determine the dielectric and piezoelectric properties of $Ba_{0.8}Sr_{0.2}Ti_{1-x}Sn_xO_3$ ($0 \leq x \leq 0.10$).

3. To correlate between microstructure, electrical and piezoelectric properties of $Ba_{0.8}Sr_{0.2}Ti_{1-x}Sn_xO_3$ ($0 \leq x \leq 0.10$).

1.5 Scope of study

The scope of this research is to study the $BaTiO_3$ based energy harvester material for the replacement of PZT. The research will focus on Sn doped barium strontium titanate (BST) with formula $Ba_{0.8}Sr_{0.2}Ti_{1-x}Sn_xO_3$ for x = 0, 0.02, 0.04, 0.06, 0.08 and 0.10. The sample will be prepared using the conventional solid-state reaction method. Then, X-ray Diffraction is used to get the phase purity of Sn doped BST. Instead, all the samples will be characterised to correlate between electrical properties, piezoelectric properties, and surface morphology by varying sintering temperature at 1400 ºC and 1450 ºC. The

effect of small doping on BST can therefore be concluded whether it can enhance its piezoelectric and dielectric properties.

1.6 Thesis structure

This thesis is arranged with several chapters starting with chapter 1, which includes a brief overview of piezoelectric mechanism, current problem statement regarding piezoelectric material for energy harvester and objectives of this research. Chapter 2 is the literature review related to this research. Several subtopics have been discussed, which is the piezoelectric materials are compared with their respective electrical and piezoelectric properties. In chapter 3 explain the methodology used to synthesise the sample and presented it through a flow chart. Chapter 4 represent the result obtained from this research, including structural analysis, impedance spectroscopy analysis, surface morphology analysis and piezoelectric analysis. Lastly, a summary and the future implementation for this project are presented in Chapter 5

CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

This chapter describes the detailed literature related to piezoelectric, including its material, the applications, and the current issue. Numerous research for enhancing the electrical and piezoelectric properties of lead-free material was previously reported in the literature. The piezoelectric effect has helped to improve our technology by producing various applications like sonar, energy harvester, and actuator. However, several issues have taken back the advantage of it. Most commercial piezoelectric material is made up of a large amount of lead (Pb). This large amount of Pb used in our daily life can be harmful to human and the environment. Pb is one of the materials that creates hazard while processing that potentially becomes toxic to the environment. Thus, the lead-free piezoelectric material is interesting for researchers to have a material with comparable properties with lead.

2.2 Piezoelectricity

Piezoelectricity comes from the Greek word “piezen”, meaning to press or squeeze. The piezoelectric effect was found in 1880 by Jacques and Pierre Curie. They found that some materials like quartz, topaz, and zincblende can generate electrical energy when mechanical force is applied, or these phenomena call the direct piezoelectric effect. The contrast of it is called a converse piezoelectric effect where the mechanical force is produced when an electric current is applied that was mathematically deduced from fundamental thermodynamic principles by Gabriel Lippmann and been confirmed by Curie brothers soon after that (B. Jaffe, W. R. Cook, 1971).

According to B. Jaffe, W. R. Cook, H. Jaffe, there is three significant sources to discover the high piezoelectric effect in ceramic material. First is the discovery of high permittivity or also known as dielectric constant. Second, the discovery of a high dielectric constant is due to ferroelectricity. Ferroelectricity was first discovered in Rochelle salt in 1921 after piezoelectricity was found. It followed with the first ferroelectricity born in ceramic materials ($BaTiO_3$) in the 1940s (Haertling, 1999). Thus, it is ushering in a new class of ferroelectric with the ABO_3 perovskite structure. $BaTiO_3$ at that time produced a high dielectric constant (ε_r = 1200 at room temperature) and used in capacitor technology up until now. The third was discovering the poling method in which the high voltage was necessary to reverse electrical moments of the ceramics' spontaneous polarised area.

Presently, many companies have commercialised piezoelectric materials for various uses, as shown in Table 2.1. It was observed that most of the commercial material used in piezoelectric technologies such as lead zirconate titanate (PZT), barium lead titanate (BPT), lead meta niobate ($PbNb_2O_6$), lead titanate (PT), bismuth sodium titanate (BNT) and bismuth titanate ($BiTiO_3$). Lead zirconate titanate (PZT) has the highest piezoelectric constant among the other materials. However, the use of lead has been restricted by Restriction of Hazardous Substances (RoHS) due to high toxicity that can cause harm to the universe

Table 2.1 List of commercial material with dielectric constant, piezoelectric constant, piezoelectric voltage constant, Curie temperature and applications

Company	**Material**	**Dielectric constant, ε_r**	**Piezoelectric constant, d_{33} (pC/N)**	**Piezoelectric voltage constant, g_{33} (mV/N)**	**Curie temperature, T_c (°C)**	**Applications**	**Reference**
APC International Ltd.	Lead zirconate titanate (PZT)	1900	400	24.8	360	High performance transducers for medical imaging applications	(*APC Materials* | *APC Materials* | *Table*, 2021)
	Lead zirconate titanate (PZT)	1450	360	27	345	Microphones and vibration pickups with preamplifier	(*Piezoceramic Materials*, 2021)
Physik Instrumente (PI) GmbH & Co. KG	Bismuth sodium titanate (BNT)	750	120	15	190	Ultrasonic transducer	
	Barium lead titanate (BPT)	950	120	-11.9	150	Sonar and hydroponic	