

**POTASSIUM SODIUM NIOBATE FORMULATION
AND COLD ISOSTATIC PROCESS FOR
IMPROVE PIEZOELECTRIC PROPERTIES**

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AND COLD ISOSTATIC PROCESS FOR
IMPROVE PIEZOELECTRIC PROPERTIES**

by

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LIST OF SYMBOLS

d_{33}	Piezoelectric charge constant
E_c	Cohesive field
ϵ	Dielectric permittivity
k_p	Electromechanical coupling coefficient
n	Refraction index
s	Second
$\tan \delta$	Tangent Loss
T_c	Curie temperature
λ	Wave length
ρ	Density

LIST OF ABBREVIATIONS

CIP	Cold Isostatic Pressing
EDX	Energy Dispersive X-ray
$K_{0.5}Na_{0.5}NbO_3$ (KNN)	Potassium sodium niobate
KN	Potassium niobate
KNN 0 CIP	Potassium sodium niobate applied with 0 MPa of CIP Pressure
KNN 100 CIP	Potassium sodium niobate applied with 100 MPa of CIP Pressure
KNN 150 CIP	Potassium sodium niobate applied with 150 MPa of CIP Pressure
KNN 200 CIP	Potassium sodium niobate applied with 200 MPa of CIP Pressure
KNN 250 CIP	Potassium sodium niobate applied with 250 MPa of CIP Pressure
KNN 300 CIP	Potassium sodium niobate applied with 300 MPa of CIP Pressure
KNN 350 CIP	Potassium sodium niobate applied with 350 MPa of CIP Pressure
KNN-LTS	$(Li_{0.035}(Na_{0.5}K_{0.5})_{0.965}(Nb_{0.86}Sb_{0.08}Ta_{0.06})O_3$
NN	Sodium niobate
PEH	Piezoelectric Energy Harvester
PZT	Lead zirconate titanate
RoHS	Restriction of Hazardous Substances
WEEE	Waste Electrical and Electronic Equipment Regulation
XRD	X-ray diffraction
ICDD	International Centre for Diffraction Data
PVA	Poly(vinyl alcohol)
wt. %	Weight percent
BFC	$BiFe_{0.8}Co_{0.2}O_3$
LS	$LiSbO_3$

FORMULASI KALIUM NATRIUM NIOBAT DAN PROSES ISOSTATIK SEJUK UNTUK MENINGKATKAN SIFAT PIEZOELEKTRIK

ABSTRAK

Sebatian berasaskan plumbum seperti $Pb(Zr_{1-x}Ti_x)O_3$, (PZT) adalah seramik piezoelektrik yang telah dibangunkan secara meluas sebagai penjana tenaga piezoelektrik (PEH) kerana sifat elektromekaniknya yang cemerlang. Walau bagaimanapun, bahan berasaskan plumbum yang digunakan pada peralatan elektrik dan elektronik menjadi sumber bahan buangan bertoksik (Pb) yang boleh menjejaskan kesihatan alam sekitar dan manusia. Suhu Curie yang tinggi, sifat piezo dan ferroelektrik yang baik bagi kalium natrium niobat menjadikannya bahan yang menarik sebagai alternatif untuk menggantikan seramik piezoelektrik berasaskan plumbum yang sedia ada. Walau bagaimanapun, kelemahan utama $K_{0.5}Na_{0.5}NbO_3$ (KNN) ialah sukar untuk menghasilkan bentuk yang padat apabila disediakan melalui kaedah pensinteran biasa. Hasilnya sentiasa mencipta pemeruapan tinggi Na_2CO_3 dan K_2CO_3 apabila terdedah pada suhu terlalu tinggi yang menyebabkan ketumpatan mula berkurangan dan kemerosotan sifat dielektrik dan piezoelektriknya. Dalam kajian ini, kesan tekanan pepadatan Isostatik Penekanan Sejuk (CIP) semasa proses pembentukan sampel-sampel KNN tulen (Tahap 1), kerjasama antara Li^+ , Ta^{5+} , dan Sb^{5+} dengan sampel KNN (KNN-LTS) (Tahap 2) dan pendopan Sr^{2+} di tapak A sampel KNN-LTS (Tahap 3) telah diselidiki. Sampel telah disediakan melalui kaedah tindak balas keadaan pepejal. Bahan-bahan mentah adalah K_2CO_3 , Na_2CO_3 dan Nb_2O_5 telah dicampur melalui campuran basah selama 24 jam menggunakan pengisar bebola menggunakan bebola ZrO_2 dalam medium etanol kemudian dikeringkan dan dikalsin pada suhu $850\text{ }^\circ\text{C}$ selama 4 jam. Sampel KNN tulen (Tahap 1) ditekan secara manual

pada tekanan 95 MPa untuk membentuk pelet dan kemudiannya semua pelet ini dipadatkan semula menggunakan CIP masing-masing pada tekanan 100, 150, 200, 250, 300 dan 350 MPa dan seterusnya disinter pada 1080 °C selama 2 jam. Analisis XRD menunjukkan bahawa peralihan struktur fasa dari fasa ortorombik ke fasa tetragonal diperoleh pada tekanan CIP 300 MPa sebagai tekanan yang optimum. Peralihan ini bertanggungjawab untuk peningkatan sifat piezoelektrik sampel dengan nilai optimum yang diperoleh daripada sampel CIP pada 300 MPa ($d_{33} = 138 \text{ pC / N}$, $k_p = 0.36$, $\rho = 4.17 \text{ g / cm}^3$). Sampel juga menunjukkan saiz butiran seragam (1.0-2.5 μm) dan sifat dielektrik yang lebih baik ($\epsilon_r = 702$ dan $\tan \delta = 0.38$). Oleh itu, KNN yang menggunakan CIP pada 300 MPa digunakan untuk kajian berikutnya. Untuk Tahap 2, KNN didop dengan jumlah yang tetap bagi element Li^+ , Ta^{5+} dan Sb^{5+} untuk meningkatkan sifat piezoelektriknya dan kemudiannya disinter pada suhu 1130 °C selama 2 jam. Analisis XRD menunjukkan bahawa puncak mewakili fasa ortorombik-tetragonal diterbalik menjadi fasa ortorombik selepas Li^+ , Ta^{5+} , dan Sb^{5+} tersebar ke dalam sistem KNN. Pemerhatian FESEM menunjukkan saiz butiran telah menurun kesan daripada penambahan dopan Li^+ , Ta^{5+} , dan Sb^{5+} . Pada 1 MHz, pemalar dielektrik KNN-LTS menunjukkan peningkatan ($\epsilon_r = 2222.48$) dan $\tan \delta$ (1.07). Sampel-sampel ini juga menunjukkan nilai yang lebih tinggi pemalar cas piezoelektrik ($d_{33} = 194 \text{ pC/N}$) dan pekali pepasang elektromekanikal ($k_p = 0.3817$). Dalam Tahap 3, KNN-LTS didopkan dengan pelbagai jumlah Sr^{2+} ($x = 0, 0.005, 0.01, 0.02, 0.03, 0.05$ and $0.10 \text{ mol } \%$) bagi meningkatkan sifat-sifat dielektrik dan piezoelektrik ke nilai maksimum. Keputusan menunjukkan jumlah optimum Sr^{2+} (0.01 mol%) di tapak A menyumbang kepada sifat-sifat dielektrik dan piezoelektrik yang cemerlang untuk seramik KNN-LTS. Pemerhatian FESEM terhadap KNN-LTS didop dengan 0.01 mol% Sr^{2+} tapak A menunjukkan saiz butir menjadi lebih besar (2.0-5.0 μm) dan

meningkatkan ketumpatan sampel (4.48 g/ cm³). Sampel KNN-LTS yang didop 0.01 mol% Sr²⁺ di tapak A mengalami sifat piezoelektrik tertinggi, $d_{33} = 345$ pC/ N dan $k_p = 0.4835$) dan sifat dielektrik yang munasabah ($\epsilon_r = 3940$, $\tan \delta = 1.8$). Oleh itu, pendopan Sr²⁺ telah berjaya meningkatkan sifat piezoelektrik sistem KNN-LTS.

POTASSIUM SODIUM NIOBATE FORMULATION AND COLD ISOSTATIC PROCESS FOR IMPROVE PIEZOELECTRIC PROPERTIES

ABSTRACT

Lead-based compounds such as $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) are piezoelectric ceramics that have been developed extensively for piezoelectric energy harvester (PEH) because of their outstanding electromechanical properties. However, these Pb-based materials that being used for electrical and electronic equipment become a source of waste materials that containing toxic (Pb) which can affect the environmental and human health. The high Curie temperature and good piezo and ferroelectric properties of potassium sodium niobate with common formula $(\text{K}_x\text{Na}_{1-x})\text{NbO}_3$ or KNN made it to be considered as a fascinating material as an alternative or to replace the existing Pb lead-based piezoelectric ceramic. However, $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) exhibits a major drawback which is difficult to produce a fully dense shape when fabricated via ordinary sintering method. It is always creating a high volatilisation of Na_2CO_3 and K_2CO_3 when exposed at high temperature which caused density start to decrease and resulting the reduction of dielectric and piezoelectric properties. In this study, the effects of Cold Isostatic Pressing (CIP) compaction pressure during shaping of pure KNN (Stage 1), Li, Sb, Ta incorporation with KNN sample (KNN-LTS) (Stage 2) and Sr^{2+} doped at A-site of KNN-LTS samples (Stage 3) were investigated. The samples have been prepared by solid state reaction method. Starting raw materials of K_2CO_3 , Na_2CO_3 and Nb_2O_5 were wet mixed for 24 hour by ball mill using ZrO_2 balls in ethanol medium then dried before being calcined at $850\text{ }^\circ\text{C}$ for 4 hours. Pure KNN samples (Stage 1) were pressed at 95 MPa using hand press to form pellets and these pellets

were re-compacted at 100, 150, 200, 250, 300 and 350 MPa, respectively using CIP and were sintered at 1080 °C for 2 hours. XRD analysis shows that the structural phase transition from orthorhombic phase to tetragonal phase was obtained from 300 MPa as the optimum CIP pressure. This transition is responsible for the enhancement of their piezoelectric properties with optimum value obtained from sample CIPped at 300 MPa ($d_{33} = 138$ pC/N, $k_p = 0.36$, $\rho = 4.17$ g/cm³). The samples also show the uniform grain size (1.0-2.5 μ m) and better dielectric properties ($\epsilon_r = 702$ and $\tan \delta = 0.38$). Thus, KNN CIPped at 300 MPa used for further investigation in the next experimental stages. In Stage 2, KNN were doped with fixed amount of Li⁺, Ta⁵⁺ and Sb⁵⁺ dopants in order to enhance the piezoelectric properties. The samples then sintered at 1130 °C for 2 hours. The XRD analysis represents that the peak of orthorhombic-tetragonal phase KNN reversed become become orthorhombic symmetric after Li⁺, Sb⁵⁺ and Ta⁵⁺ diffused into the KNN system. The FESEM observation shows the grain size has decrease as addition of Li⁺, Sb⁵⁺ and Ta⁵⁺ dopants. At 1 MHz, the dielectric behavior of KNN-LTS show increasing dielectric permittivity ($\epsilon_r = 2222.48$) and lower $\tan \delta$ (1.07). This sample also shows high piezoelectric charge constant ($d_{33} = 194$ pC/N) and electromechanical coupling coefficient ($k_p = 0.3817$). In Stage 3, KNN-LTS were doped with various amount of Sr²⁺ ($x = 0, 0.005, 0.01, 0.02, 0.03, 0.05$ and 0.10 mol%) to enhance their dielectric and piezoelectric properties. The results showed that the optimum amount of Sr²⁺ (0.01 mol%) at the A-site KNN-LTS contributed to the excellent dielectric and piezoelectric properties for KNN-LTS ceramics. The FESEM observation on KNN-LTS doped with 0.01 mol% of Sr²⁺ at the A-site shows the grain size become larger (2.0-5.0 μ m) and improve the density of the sample (4.48 g/ cm³). The Sr²⁺ doped KNN-LTS sample with 0.01 mol% of Sr²⁺ dopant at A-site experience the highest piezoelectric properties ($d_{33} = 345$ pC/ N and $k_p = 0.4835$) and dielectric

properties ($\epsilon_r = 3940$, $\tan \delta = 1.8$). Therefore, Sr^{2+} doping is successfully improved the piezoelectric properties of KNN-LTS system.

CHAPTER ONE

INTRODUCTION

1.1 Background

Ceramic materials have contributed for the development and civilization of human being since prehistoric. Previously, ceramics were widely used for artificial expression, household purposes and also as structural materials. However, ceramic materials for the past few decades become a major player for the technological applications advancement. The development of ceramic materials from traditional ceramics (clay-based) to advanced ceramics (high purity and homogenous synthesized raw materials) have expanded especially in advanced technology fields. This advancement is mainly driven by researchers to fulfil the new and better materials properties which known as smart materials. Smart materials represent the materials that undergo transformation through physical interactions. The list of smart materials invented or discovered keep on increasing and piezoelectric is listed as one of the prominent smart materials. Nowadays, piezoelectric materials play a major role in numerous applications in our life and have been recognised as special material among other smart materials (Graham et al., 2004).

Piezoelectric materials are a group of materials that develops a dielectric displacement (or polarization) when placed under load which is known as the “direct piezoelectric effect”. The “inverse piezoelectric effect” were happened when piezoelectric materials are applied directly by a voltage which caused its dimension change (Jordan & Dunajes, 2001). Piezoelectric materials can be divided into two groups: crystals and ceramics. Crystal is a solid materials whose constituents (such as

atom, molecules or ions) are arranged in a highly ordered microscopic structure, forming a crystal lattice that extends in all directions. The best known piezoelectric material in the crystal group is quartz (SiO_2), the trigonal crystallized silica is familiar as one of the most regular crystals on Earth's surface. Ceramics is an inorganic, non-metallic solid that is prepared from powder materials and is fabricated into products through application of heat. Ceramics made up of two or more elements which is called a compound. Ceramics made up of many varied crystal structures which results in a very wide range of properties. Barium titanate (BaTiO_3), lead titanate (PbTiO_3), lead zirconate titanate (PZT) and $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN as a lead-free piezoelectric material) are the typical piezoelectric materials in the ceramic group. The piezoelectric materials such as BaTiO_3 , PZT, PbTiO_3 and KNN are not naturally guaranteed as piezoelectric but somewhat exhibit a polarized electrostatic effect. Some piezoelectric materials not guaranteed exhibit as piezoelectric but the materials slightly relatively shift to the positive and negative electric charge in opposite directions which exhibit a polarized electrostatic effect which is within an insulator or dielectric which can be induced by an external electric field. To exhibit truly piezoelectric properties, a material must be made as a single crystal. Ceramic is composed up from multi-crystalline structures consisting of the huge members of randomly oriented crystal grains (Qinhua, 2013).

The random orientation of the grains needed a poling treatment in order to activate the piezoelectric properties of ceramics. The poling treatment will be forcing the ions to be aligned along the poling axis (Philipp et al., 2012). Among ceramic piezoelectric materials, PZT-based materials are vastly studied due to their superior piezoelectric performance (Sedano et al., 2004; Ng and Liao, 2005; Koyama et al., 2009). However, as a lead-based material, PZTs have inherent various problems due to their toxicity and are also hazardous to the environment. Therefore, extensive researches are geared towards