UNIVERSITI TEKNIKAL MALAYSIA MELAKA

EFFECT OF PRASEODYMIUM (III) OXIDE (Pr_2O_3) DOPED BISMUTH SODIUM TITANATE-BARIUM TITANATE (BNT-BT) VIA SOLID STATE REACTION

This report submitted accordance with the requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials)

By

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2015

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

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TAJUK: **Effect of Praseodymium (III) Oxide (Pr_2O_3) Doped Bismuth Sodium Titanate-Barium Titanate (BNT-BT) Via Solid State Reaction**

SESI PENGAJIAN: **2014/15 Semester 2**

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APPROVAL

This report is submitted to the Faculty of Engineering Manufacturing of UTeM as a partial fulfillment of the requirement for the degree of Bachelor's Degree in Manufacturing Engineering (Materials) with Honours.

The member of the supervisory is as follow.

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(Prof. Madya Dr. Mohd Warikh Bin Abd Rashid)

ABSTRAK

Seramik piezoelektrik dikenali sebagai seramik termaju yang menukarkan isyarat input untuk menyediakan maklum balas haptik. Sambutan teguh kepada penggunaan kuasa yang lebih rendah dan bersaiz kecil membuat seramik piezoelektrik bahan yang sesuai dalam pelbagai aplikasi. Seramik piezoelektrik diperbuat daripada bahan-bahan mentah yang paling selamat yang mesra pengguna dan mesra alam sekitar. Tujuan projek ini adalah untuk mengkaji tindak balas Pr-didopkan BNT-BT seramik dengan menggunakan tindak balas keadaan pepejal. $BaTiO_3$ (BT) adalah terkenal dengan bahan feroelektrik bebas plumbum dengan struktur perovskit yang menawarkan dielektrik yang baik dan sifat-sifat piezoelektrik tetapi suhu Curie agak rendah, Tc = 120 ° C. $BiNaTiO_3$ (BNT) adalah bahan feroelektrik perovskit yang kuat pada suhu bilik dengan suhu Curie tinggi, Tc = 320 ° C, polarisasi remanent Pr = 38μC / cm^2 dan bidang paksaan Ec = 73kV / cm. Untuk menggunakan seramik piezoelektrik BT berasaskan bebas plumbum, meningkatkan suhu Curie adalah perlu untuk peralihan fasa tetragonal ke orthorhombic. Dengan menggunakan tindak balas keadaan pepejal, ia menyediakan proses pensinteran lebih cepat dan juga untuk resapan atom lebih cepat daripada proses keadaan pepejal serentak. Tarikan kapilari kerana membasahkan cecair memberikan pemadatan padat cepat tanpa memerlukan tekanan luaran. Cecair juga mengurangkan geseran antara zarah, dengan itu membantu penyusunan semula pesat zarah pepejal. Kawalan saiz butiran adalah mungkin semasa tindak balas keadaan pepejal.

ABSTRACT

Piezoelectric ceramics are known as advance ceramics that convert the input signal to provide a haptic feedback. The fast response to lower power consumption and small in size make piezoelectric ceramics an ideal material in a wide range of applications. The piezoelectric ceramics are made from the safest raw materials that are user friendly and environmental friendly. The aim of this project is to study the reaction of Pr-doped BNT-BT ceramic by using solid state reaction. $BaTiO_3$ (BT) is a well-known lead-free ferroelectric material with perovskite structure which offer good dielectric and piezoelectric properties but relatively low Curie temperature, Tc=120°C. $BiNaTiO_3$ (BNT) is a strong perovskite ferroelectric material at room temperature with high Curie temperature, Tc=320°C, remanent polarization Pr=38μC/cm^2 and coercive field Ec=73kV/cm. In order to use BT based lead-free piezoelectric ceramics, it is necessary to increase the Curie temperature and shift the orthorhombic to tetragonal phase transition. By using the solid state reaction, it provides faster sintering process and also for faster atomic diffusion than the concurrent solid state processes. The capillary attraction due to the wetting of liquid gives rapid compact densification without the need for an external pressure. The liquid also reduces the inter-particle friction, thereby aiding rapid rearrangement of the solid particles. Grain size control is possible during solid state reaction.

DEDICATION

This thesis work is dedicated to my supervisor and colleagues who have been a constant source of support and encouragement during the challenges of graduate school and life. I am truly thankful for having you in my life. This work is also dedicated to my parents, who have always loved and pray for me unconditionally and taught me to work hard for the things that I aspire to achieve.

ACKNOWLEDGEMENT

In the Name of Allah, the Most Merciful, the Most Compassionate all praise be to Allah, the Lord of the worlds and prayers and peace be upon Muhammad SAW, his servant and messenger.

First and foremost, I thank Allah SWT for letting me live to see this thesis through. I would like to place my deep sense of gratitude to Prof. Madya Dr Mohd Warikh Bin Abd Rashid, Dept. of Engineering Materials, UTeM, for his generous guidance, help and useful suggestion.

I express my sincere gratitude to Dr. Umar Al-Amani Bin Haji Azlan, Dept. of Engineering Technology, UTeM, for his simulating guidance, continuous encouragement and equipment throughout the course of present work.

I am extremely grateful to the UTeM staff especially the Engineering Material Dept. staff for their insightful comment and constructive suggestion to improve the quality of this research work.

I am thankful to Maziati Akmal, Azuwa and my entire classmates for their valuable suggestion and discussion at every step of my research work.

Finally, I am forever indebted to my parents, sisters, and brothers for their blessings, love, inspiration, encouragement, and strong supports in every moments of my life.

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ABBREVIATION

$BaTiO_3$	Barium Titanate
Bi Na)TiO_3	Bismuth Sodium Titanate
BNT-BT	Bismuth sodium titanate- barium titanate
DSC	Differential scanning calorimeter
FTIR	Fourier Transformation Infra-Red
HIP	Hot Isotactic Pressure
LCR	Inductance, Capacitor and Resistant
P	Polarization
PrO_2	Praseodymium Oxide
PZT	Lead zirconate titanate
REE	Rare Earth Element
RoHS	Restriction of the use of certain Hazardous substances in electrical and electronic equipment
SEM	Scanning Electron Microscope
SSR	Solid State Reaction
T_c	Curie temperature
WEEE	Waste Electrical and Electronic Equipment
XRD	X-ray diffusion

CHAPTER 1

INTRODUCTION

This section basically tells the project ideas on the previous work. On the other hand, the improvement and innovation made on certain processing route to achieve good uniformity in term of microstructure and also increased piezoelectric properties itself.

1.1 Introduction

Ceramics are defined as the solid compounds that consist of metallic and nonmetallic elements which are formed by the application of heat or pressure or both. In general, most ceramics have brittle, hard, wear resistant, nonmagnetic, chemically stable, thermal and electrical insulators properties. Nowadays, ceramics materials are used everywhere and there are always new ceramics materials invention to fulfill the demands. Ceramics materials properties depend on the types of atoms packed. The most common ceramic materials bonding are covalent and ionic bonding which is different from metal that have sea of electron that have very good electrical conductivity.

Most of the ceramic materials are dielectrics that possess very low electrical conductivity but supports electrostatic field. Electrical conductivity of ceramics varies with the temperature and force. Ceramic materials have high dielectric strength and high dielectric constant, which the dielectric ceramic materials are used in manufacturing capacitors, insulators and resistors for electronic devices. The dielectrics are electrical insulating materials, which can be polarized.

Today, piezoelectric ceramics is the solutions used to convert the input signal to provide feedback. It is often used in mobile to provide feedback. The fast response with low power consumption, and small size ensure the piezoelectric is ideal in electrical devices such as sensors and mobile devices.

Piezoelectricity is electricity resulting from compression. In Greek word the piezoelectric is piezo or piezein which means to squeeze or press electric or electron, which means amber, an ancient source of electric charge in the other terms where the electric charge that accumulates in certain solid materials such as crystals, certain ceramics, and biological matter, in response to applied mechanical stress. Piezoelectricity was discovered in 1880 by French physicists Jacques and Pierre Curie (Jordan and Ounaies, 2001).

The linear electromechanical interaction between the electrical state and mechanical in crystalline materials with no upturn symmetry which means internal generation of electrical charge resulting from force applied is the piezoelectric effect. The nature of the piezoelectric effect is closely related to the occurrence of electric dipole moments in solids.

The change of polarization (P) when applying a mechanical stress is piezoelectric effect caused either by a reconfiguration of the reorientation of molecular dipole moments under the influence of the external stress or by dipole-inducing surrounding. Piezoelectricity may then visible in a variation of the polarization strength, its direction or both, with the details depending on the orientation of P within the crystal, crystal symmetry and the applied mechanical stress. A variation of surface charge density upon the crystal faces due to the change in P. In converse piezoelectric effect, the application of an electrical field creates mechanical deformation in the crystal.

Piezoelectric effects have been discovered for its present in varieties of applications such as loudspeaker and signal transducer. Therefore, the piezoelectric ceramic is developed where the barium titanate ($BaTiO_3$) adopts piezoelectric characteristic on a useful scale when electric field is applied.

There are many ways to improve materials properties to gain certain properties and among the ways is doping, purposely insert the impurities into an intrinsic semiconductor especially to modulate its electrical properties. So, material selection for the doping agent is the crucial matter to ensure the electrical properties can be controlled and to make the doping more efficient and better conductivity can be developed. Thus, rare earth element is chosen as the dopant agent due to the most suitable dopant that can control the properties according to the needs. Rare earth is transition element where any of a group of chemically similar metallic elements comprising the lanthanide series with scandium and yttrium, and they tend to occur together in nature and difficult to separate from one another.

In order to fabricate piezoelectric ceramic, usually solid state technique is applied. There are two types of solid state methods, firstly is sintering or powder blending and consolidation, where the powder and discontinuous reinforcement are mixed and then bonded and secondly is diffusion bonding, where several layers are sandwiched before pressed to form a matrix.

Diffusion bonding type use the roll bonding or wire/fiber winding that only used to fabricate simple shape parts such as tubes and plates. In roll bonding, process of combined strips of two different material resulted in formation of a laminated composite material while wire/fiber winding is a process of combined winding continuous ceramic fibers and metallic wires followed by pressing at elevated temperature.

Therefore, by doping with the rare earth element using a solid state technique in producing piezoelectric not only adequate to do the job but also efficient in electrical, thermal and mechanical properties of piezoelectric will be produced.

1.2 Problem Statement

Nowadays, rare earth elements (REE) have been used for doping other elements to achieve better properties especially in the electrical properties. Furthermore, by choosing the REE as dopant, it can lower the surface energy thus make the surface-active agent, can combined the grain boundary to stabilize the boundary and restrain the sliding of boundaries, remove the impurities and thus improve the performance (Min et al,. 2007). Beside that, by choosing the doping with REE will leads to the beneficial effects on magnetic characteristics, the reduction in flux jumps and increasing the thermal stability (Lowhorn et al,. 2005).

The standardization of the process parameters resulted in a good properties, the percentage of doping should not be more than one percent (Min et al,. 2007), if not it would be called as addition or mixture. Besides that, the doped atom must be same position as the semiconductor atom position and there should be no distortions in the crystal after the insertions of dopants. Furthermore, the dopants size should be exactly same as the atom crystal size. There are two basic techniques in doping where by heating or bombarding. In heating, the semiconductor crystal is heat up at atmosphere condition and dopants diffusion take place in lattice site of crystal where in bombarding, the semiconductor is bombarded with the ions of semiconductor itself and the dopants will be embedded.

However, in recent years, the needs in developing lead-free piezoelectric materials are increasing due to the environmental issues on hazardous substances. According to Waste Electrical and Electronic Equipment (WEEE) and Restriction of the use of certain Hazardous substances in electrical and electronic equipment (RoHS), large amount of lead must be eliminated in order to protect human health as well as environment by exclusion or substitution of hazardous substances used in electric and electronic devices. Thus, BNT-BT (Bismuth sodium titanate- barium titanate) is selected as the ceramic materials due to lead-free ceramics due to very good result due to its well-balanced properties of piezoelectric and gives no harmful environmental effects.

Generally, piezoelectric ceramic have been fabricated using conventional solid state (Muralidharan et al,. 2010). In order to produce the piezoelectric ceramic with high quality that brings positive effect, the solid state technique needs to be justified either the diffusion bonding or sintering. Thus several parameters must be considered such as the result of bonding matrix metal and dispersed phase due to mutual diffusion occurring between materials in solid states at elevated temperature under certain pressure.

There are piezoelectric generators, sensors, piezo actuators, and transducers. Piezoelectric ceramics can generate voltages sufficient to spark across an electrode gap, that can be used as igniters, a piezoelectric sensor converts a physical parameter into an electrical signal, a piezoelectric actuator converts an electrical signal into a precisely controlled physical displacement, to finely adjust precision machining tools, lenses, or mirrors and piezoelectric transducers convert electrical energy into vibrational mechanical energy.

There are several problems which limit the piezoelectric application where BT has a disadvantage which is relatively low Curie temperature ($T_c \sim 120°C$), leading to poor temperature stability and solid phase sintering is normally used at high sintering temperature, by introducing the novel route of Solid State Reaction (SSR) can lower the sintering temperature added with sintering aids.

With the increasing demand in manufacturing non-hazard product, lead free piezoelectric ceramic is develop by contribute the doping of Praseodymium oxide with BNT-BT using the solid state technique in producing high quality and environmental friendly piezoelectric ceramics thus provide details understanding in the rare earth properties that suited to be doping agent.

1.3 Objective

Several objectives are listed as follows:

i.) To prepare the BNT-BT samples via solid state reaction.

ii.) To investigate the effect of Barium Titanate ($BaTiO_3$) and Bismuth Sodium Titanate $(BiNa)TiO_3$ doping with Praseodymium Oxide (PrO_2).

iii.) To investigate the dielectric loss of Pr doped BNT-BT.

1.4 Scope

Generally, this work is more focused on synthesis of BNT-BT doped with Pr by using the SSR. In order to improving the properties of BNT-BT ceramics material, the method of processing to stimulate the doping factor to be stable during sintering process is varied by their doping mass percentage.

In SSR, the fine powder is produce using the planetary ball milling where the materials will be grind and mixing together to extremely fine powders. Balls are used as grinding media where it is rotated in the ball mill that consist of a hollow cylindrical shell rotating about its axis. The solid particle lies between the balls are grind by the impact and reduced in size. Then, the fine powder will be compounded in the uniaxial press. The uniaxial press will give pressure in pressure container vessel. The compound is sintered before analysed the ability of the Pr doped by BNT-BT and the other properties that effected in using Pr as dopant. The material is treating to high temperature with fire without melting it to liquid form. Other than diffusing the particles together, sintering stage is the shaping process for the materials with extremely high melting points to get the compound in shape. After sintering process, the characterization process is applied to analyse the effect of rare earth doped in piezoelectric ceramic in term of mechanical, physical and electrical properties. Scanning electron microscope (SEM), X-ray diffusion (XRD), and Raman spectroscopy, Fourier Transformation Infra-Red (FTIR) and LCR test is used to analyse the mechanical, physical and electrical properties of the piezoelectric ceramic.

To identify the suitable and best method of processing Bismuth Sodium Titanate $(BiNa)TiO_3$ doping with $BaTiO_3$ (BT). The comparison sticks with the parameters value which is Curie temperature, dielectric constant and percentage of sintering aid. Sample should be tested by using standard to produce accurate result which can be then compare obtained value with others process. Faster calcination SSR low temperature added with sintering aid is believed to have good electrical properties.

CHAPTER 2

LITERATURE REVIEW

This section generally tells about the previous research regarding to the piezoelectric properties which is subjected to BNT-BT. Furthermore, the doping element is the preliminary study in order to improve the microstructure of the ceramic compound.

2.1 Piezoelectric

Piezoelectric is electricity resulting from pressure that defined from Greek word, piezo and piezin which means press and electric that was discovered by Pierre Curie and Jacques, French physicists (Jordan and Ounaies, 2001). Gabriel Lippmann has discovered the converse piezoelectric effect in 1881 through the mathematical theory. Today, piezoelectric ceramics is the innovation that solves the haptic fast response with a small size, and low power consumption. It was reported that a mechanical stress was applied on the crystals to produce the electric and the voltage of these electrical charges was proportional to the stress.

The piezoelectric material is significant quantity of electric dipoles that can either induced by molecular groups or by ions on crystal lattice sites with asymmetric charge surrounding. A dipole is a vector sum of a direction and a value of electrical charges that tends to have same direction when close to each other, and form regions called Weiss domains (Chaiyo et al., 2011). Generally, the poling process is applied across the material to ensure the domains are aligned.

Piezoelectric materials exhibit intrinsic, called as spontaneous polarization. Usually piezoelectric ceramics are polycrystalline materials that divided into regions with similar polarization. The domains produce a net polarization when they are aligned together and when the electric field is applied, the dipoles can contract or expand. If a strain is applied, the dipoles are again forced to contract or expand, this time producing a potential difference (Lin et al., 2010).

Piezoelectric materials are applied as igniters, displacement transducer, actuators, and generators of ultrasonic energy. Arrays of piezoelectric elements have been used to produce ultrasonic imaging equipment (Adachi et al., 2010). The piezoelectric effect of natural monocrystalline materials is relatively small such as quartz and Rochelle salt. Barium titanate ($BaTiO_3$) and lead zirconate titanate (PZT) are polycrystalline ferroelectric ceramics that induce larger electric voltages. Special doping makes it possible to optimize the piezoelectric and dielectric parameters of the ceramics.

The sources of polarization are electronic polarization, ionic polarization, orientation polarization, space charge polarization and domain wall polarization (Yang et al., 2009). The displacement of electron cloud by an electric field will formed the electronic polarization in all dielectric materials (Yang et al., 2009).

In this new era, people concerns the health condition and environment condition in their daily life routine and same goes to piezoelectric ceramics. According to Restriction of the use of certain Hazardous substances in electrical and electronic equipment (RoHs), large amount of lead must be eliminated in order to protect human heath as well as environment by exclusive or substitution of hazardous substance used in electric and electronic devices. Thus, lead-free piezoelectric ceramics is invented with varies of desired properties according to the market demand.

When considering the electromechanical effects of piezoelectric materials, the piezoelectric charge coefficients, the piezoelectric voltage coefficients and the piezoelectric coupling factors should be the important parameters. The mechanical testing and physical testing also applied to analyse the mechanical and physical properties of the BNT-BT piezoelectric ceramics doped by rare earth element.

Later, SEM, XRD, FTIR, Raman Spectroscopy and LCR test are among the testing used to analyse the mechanical, physical and electrical properties of piezoelectric ceramic.

2.2 BNT-BT

Pure BNT is an A-site complex perovskite-structured ferroelectric material with a relative high Curie temperature (T_c = 320°C) (Chaiyo et al., 2011). BNT has a rhombohedral symmetry with strong ferroelectricity (remnant polarization P_r = 38μC/cm^2) at room temperature. However, the poling treatment for pure BNT ceramics is difficult due to its high coercive field (E_c = 7.3 kV/mm), resulting in relatively weak piezoelectric constant (d_{33}~71–80 pC/N). In order to decrease the coercive field and improve the piezoelectric property, forming BNT-BT by liquid phase sintering has been proposed and confirmed to be an effective way (Pisitpipathsin et al., 2010).

The powder morphology, grain microstructure and electrical properties are highly dependent on many parameters which are simplified to processing method, heat treatment condition and temperature, grain orientation and densification.

The processing methods influence the particle morphologies of BNT with average particle size are within the range of 10nm-50nm synthesized by a metal-organic polymeric precursor process (Lin et al., 2010). Beside that, the formation of agglomeration due to Van der Waals forces. Furthermore, high milling energy gives strong agglomeration of BNT powders.

It was reported that the microstructure of BNT powders has a plate-like structure. BNT is also known as highly anisotropic properties, whereby it is electrical dependent. Along the a-axis, the spontaneous polarization can achieve up to 50μC/cm^2, while at the c-axis does not exceed 4μC/cm^2 (Kim et al., 2007).

Moreover, besides the porosity and grain size, the orientation in a polycrystalline ceramic also effected. In order to improve the electrical properties, the preparation using magnetic alignment has outstanding merits such as easily and freely to control the direction of orientation and magnetic field among all the attempts that has been carried out (Corker et al., 2000).