EFFECT OF Li_2CO_3 ADDITION ON THE PIEZOELECTRIC AND DIELECTRIC PROPERTIES OF $Pb_{0.93}La_{0.02}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$ CERAMICS

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF SYMBOLS

k_p	Electromechanical Coupling Factor
ε_r	Dielectric Permittivity
ε_o	Permittivity Vacuum
ε''	Imaginary Component of Permittivity
ε'	Real Component of Permittivity
d_{33}	Piezoelectric Constant
$\tan\delta$	Loss Tangent
Q_m	Quality Mechanical Factor
°C	Degree Centigrade
μm	Micrometer
g	Gram
cm	Centimeter
MHz	Mega Hertz
GHz	Giga Hertz
P_r	Remenant Polarization
pC/N	Pico-Coulombs Newton
T_c	Curie Temperature

LIST OF ABBREVIATIONS

BE	Backscattered Electron
B-PZT	Pb-Ba(Zr,Ti)O_3
DTA	Differential Thermal Analysis
FESEM	Field Emission Scanning Electron Microscopy
ICDD	International Center for Diffraction Data
LBC	Li_2O-Bi_2O_3-CdO
LBO	Bi_2O_3-Li_2CO_3
MPB	Morphotropic Phase Boundary
PT	Lead Titanate
PLZT	Lead Lanthanum Zirconate Titanate
PLSZT	Lead Lanthanum Strontium Zirconate Titanate
PLSZLiT	Lead Lanthanum Strontium Zirconate Lithium Titanate
PNN-PT-PZ	$PbNi_{1/3}Nb_{2/3}O_3$-$PbTiO_3$-$PbZrO_3$
PSZT	Lead Strontium Zirconate Titanate
PZN-PZT	$Pb(Zn_{1/3}Nb_{2/3})O_3$-$Pb(Zr_{0.49}Ti_{0.51})O_3$
PZT-PZN-PMnN	$Pb(ZrTi)O_3$-$Pb(Zn_{1/3}Nb_{2/3})O_3$-$Pb(Mn_{1/3}Nb)O_3$
PZ	Lead Zirconate
PZT	Lead Zirconate Titanate
SE	Secondary Electron
TGA	Thermogravimetry Analysis
XRD	X-ray Diffractometer

KESAN PENAMBAHAN Li_2CO_3 KE ATAS SIFAT-SIFAT PIEZOELEKTRIK DAN DIELEKTRIK SERAMIK $Pb_{0.93}La_{0.02}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$

ABSTRAK

Plambum zirkonat titanat (PZT) adalah yang paling banyak diselidiki di kalangan seramik perovskite berasaskan plambum. Sifat-sifat piezoelektrik dan dielektriknya kerap diubahsuai dengan berlainan dopan. Apabila PZT di dop dengan La^{3+}dan Sr^{2+}, pemalar dielektrik (ε_r) dan pemalar piezoelektrik (d_{33}) meningkat dengan sedikit peningkatan dalam factor pengganding planar (k_p). Walau bagaimanapun, ε_r dan k_p yang tinggi adalah dikehendaki untuk peranti-peranti elektromekanikal seperti kipas piezoelektrik. Dalam penyelidikan ini, seramik $Pb_{0.93}La_{0.02}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$ (PLSZT) di dop dengan Li_2CO_3 untuk dikaji kesannya ke atas sifat-sifat piezoelektrik dan dielektrik. Seramik ini telah disintesis dengan pengisar bebola planet bertenaga tinggi di dalam udara biasa selama 40 jam dan masing-masing disinter pada suhu yang agak rendah dari 1150 °C ke 850 °C selama 3 jam. Penambahan Li_2CO_3 ke dalam PLSZT meningkatkan penumpatan seramik ini dan purata saizbutir. Maka mengukuhkan sifat-sifat piezoelektrik dan dielektrik seramik PLSZT. Nilai terbaik sifat-sifat piezoelektrik dan dielektrik PLSZT diperolehi bila di dop dengan 0.7 mol% Li^+. Ketumpatannya ialah 7.420 g/cm^3, k_p ialah 0.461, d_{33} ialah 259 pC/N, ialah 1270 dan tan δ ialah 0.084.

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ABSTRACT

Lead zirconate titanate (PZT) is the most widely investigated amongst lead-based perovskite ceramics. Its piezoelectric and dielectric properties are always modified with different dopants. When PZT doped with La^{3+} and Sr^{2+}, the piezoelectric constant (d_{33}) and dielectric constant (ε_r) are increase with slightly increase in electromechanical coupling factor (k_p). However, high k_p and ε_r is desirable for electromechanical devices such as piezoelectric fan. In this research $Pb_{0.93}La_{0.02}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$ (PLSZT) ceramic is doped with Li_2CO_3 to investigate its effect on piezoelectric and dielectric properties. The ceramic was synthesized by high energy planetary ball milling in air for 40 hours and sintered at relatively low temperatures from 1150 °C to 850 °C for 3 hour, respectively. The addition of Li_2CO_3 in PLSZT improved the densification of the ceramics and increases the average grain size. Thus, piezoelectric and dielectric properties are enhanced with the increase of Li^+ content. The best piezoelectric and dielectric properties were obtained for 0.7 mol% Li^+ doped PLSZT ceramics. The density is 7.420 g/cm^3, k_p is 0.461, d_{33} is 259 pC/N, ε_r is 1270, and tan δ is 0.084 is observed.

CHAPTER ONE

INTRODUCTION

1.1 Background

Ceramics are defined as non-metallic inorganic solids which are bonded together by multiple bonds such as ionic and covalent bond. The word ceramic is derived from Greek word “keramos” which means “potters clay”. Precisely, the word keramos is originated from the Sanskrit language which means “to burn” (Carter & Norton, 2007). On the basis of raw materials, the ceramics are classified into two classes’ i.e. traditional ceramics and advanced ceramics. Traditional ceramics are produced by naturally occurring raw materials. While advanced ceramics are synthesized by chemical processing routes or from synthetic raw materials.

Electroceramics are the advanced ceramic materials whose electrical and magnetic properties are prime focus for the applications. The history of electroceramics begins in 1940, when the Al_2O_3 were used in the spark plugs as an insulator. Nowadays, numerous materials are used in different electronic and magnetic applications. For example, zinc oxide in varistors, barium titanate in capacitors, tin oxide in gas sensors, lithium niobate in electro-optic devices and lead zirconium titanate in piezoelectric devices are commonly used (Segal, 1991).

To date, lead zirconium titanate (PZT) is one of the most widely studied electroceramics. PZT is a solid solution of the antiferroelectric lead zirconate

($PbZrO_3$), and ferroelectric lead titanate ($PbTiO_3$). It has a nearly cubic perovskite crystal structure with general formula ABO_3, where A^{2+} site contains Pb^{2+} and B^{4+} site contains Ti^{4+} and Zr^{4+} ions. The body centered B^{4+} cation is surrounded by a corner linked octahedral oxygen network. Where, A^{2+} cation is located at the corner of cubic unit (Galasso, 2013). Due to lack of center of symmetry in crystal structure, it exhibits the piezoelectric effect. By definition, piezoelectricity is an ability of the crystal to develop an electric displacement upon the mechanical stress which is also known as a direct piezoelectric effect. Piezoelectric material also undergoes mechanical deformation on the application of electric field which is known as converse effect. Ferroelectricity is a sub class of piezoelectricity in which the polarization occurs spontaneously and the dipoles can be reoriented under an applied electric field. The reorientation of polarization in a material is called poling process. Due to this poling process, the piezoelectric effect can be utilized in a ferroelectric ceramics.

Number of ferroelectric ceramics such as $BaTiO_3$, $Pb(Zr,Ti)O_3$, $PbLa(ZrTi)O_3$, PbN_2O_6 and $PbTiO_3$ are known for piezoelectric applications. In early 1940, the $BaTiO_3$ was extensively used but nowadays it is largely replaced by PZT. This is because PZT is easily poled, having high electromechanical coupling coefficient, has high Tc (Curie temperature), and has wide range of dielectric constant. These exceptional piezoelectric properties are optimum at near to the morphotropic phase boundary (MPB). MPB is the region that shows an abrupt structural change within a solid solution. The variation in composition around the MPB region greatly affects the materials property.

PZT is always modified with dopants to further improve and optimize its basic properties required for a specific application. Usually dopant is incorporated in the parent material within the concentration of ≤ 3 at.% (Haertling, 1999). Doped PZT are divided into two groups, i.e. hard PZT and soft PZT, on the basis of the effect that dopant induces on PZT. These effects are mainly depends on the charge of dopants. According to the charge they carry, the dopants are further classified into three classes i.e. acceptor, donor and isovalent. Since the discovery of the PZT, numerous dopants were added for the enhancement of piezoelectric properties e.g. Nb^{5+}(Chu et al., 2004), Gd^{3+}(Parashar et al., 2004), Sr^{2+}, La^{3+}, Li^{+}(Tiwari & Srivastava, 2015), W^{3+}(Bochenek & Zachariasz, 2015), Sm^{3+}, Nd^{3+} and rare earth elements (Eu^{3+}, Dy^{3+}, Er^{3+}, and Yb^{3+}) (Shannigrahi et al., 2004).

PZT is generally synthesized by conventional solid state reaction and sintered at high temperature around 1200 °C or above. But too high temperature is not suitable for Pb^{2+} containing materials, which is due to the high volatility of Pb^{2+}. The loss of Pb^{2+} from the PZT ceramic eventually affects the useful properties of the material such as electrical, mechanical and optical. Several attempts have been made to successfully densify the PZT material at relatively low temperature. The main approaches that have been employed for that purpose are the use of ultra fine powders and the addition of sintering aids. For ultra fine powders, the submicron or nanosized powders have been synthesized by mechanochemical alloying technique which is also known as high energy ball milling. As compared it to other processing routes, it gives several advantages. Firstly, the widely available oxides are used as the starting materials. Secondly, it is a simpler process due to single firing step. Furthermore, it takes place in a sealed container at room temperature, thus avoid the loss of volatile Pb^{2+} (Kong et al., 2008). As the Pb^{2+} loss occurred at elevated temperature, excess PbO powder intentionally added during batch preparation for two reasons. Firstly, to enhance densification by forming a PbO rich liquid during sintering process. Secondly, it is added to compensate the evaporation of PbO during calcinations and sintering (Song et al., 1989).

Piezoelectric materials especially PZT is widely used as actuators and sensors in modern technologies such as accelerometers, microphones, micromotors, and micropumps. The type of piezoelectric actuators which is used for cooling applications is known as piezoelectric fan (Liu et al., 2013). It is mainly employed in compact and portable microelectronic devices for thermal management. In electronic devices, the thermal management is an important task to prevent electronic circuit from the adverse effect of heat. Previously, the conventional cooling system, such as rotary fan and heat sink were used for thermal management in electronic devices (e.g. personal computers). In recent years, the electronic industry is moving towards the compact and portable microelectronic devices which results in generating the smaller electronic components. These compact microelectronic devices experience a heat generation. Due to constrained and small space within the electronic package, the heat removal becomes a challenge.

1.2 Problem Statement

Lead zirconate titanate (PZT) is a well known piezoelectric material in the field of electroceramics. Its exceptional piezoelectric properties made it dominant among other ferroelectric materials. It is extensively used in the wide range of electronic applications, such as in sensors, transducers, and actuators (Setter & Waser, 2000). PZT always modified with dopants for further improvising the electrical properties d_{33} (piezoelectric constant), ε_r (relative permittivity) and k_p (electromechanical coupling factor) that is required for specific application. Numerous donor dopants (Nb, Nd, La, and rear earth metals) have been added to PZT ceramics to tailoring its piezoelectric and dielectric properties. Amongst these dopants La^{3+} was extensively studied. Incorporation of La^{3+} ion produce a profound effect on dielectric properties (ε_r), due to the growth inhibition caused the degradation of k_p (Pdungsap et al., 2005; Sharma et al., 2006; Sahoo& Panda, 2013). The literature on the improvising the k_p of PZT was not clearly visible.

The k_p of piezoelectric ceramics have been studied by some researchers. Kulcsar (1959) studied the individual effect of Sr^{2+} and Ca^{2+} on electromechanical properties of the PZT. The profound effect was observed on ε_r but the k_p is only slightly increased from 0.48 to 0.51, which is attributed to the reduction in the distortion from cubic symmetry to rhombohedral. Nasar et al. (2002) had investigated theoretically and experimentally the effect of Sr^{2+} on the remanent polarization (P_r) and k_p of the PZT ceramics. The addition of Sr^{2+} minimizes the energy of rhombohedral phase, which ease the transformation of phases and hence increase the k_p value. For most of the electroceramic applications the high ε_r and k_p

are desired in combination such as for piezoelectric fan application. For this purpose PZT ceramic was co-doped with Sr^{2+} and La^{3+} by few researches. Kalem et al. (2011) studied the co-doped PZT system with Sr^{2+}, La^{3+} and varied the concentration of both dopants and Zr/Ti ratio. The author found that at a lower concentration of La^{3+}, the piezoelectric properties (k_p and d_{33}) were increased, while at a higher La^{3+} content, the k_p was decreased due to growth inhibition. In case of varying the Sr^{2+} content the k_p value was increased up to 0.56. Similar material (PZT with $La^{3+}$and Sr^{2+}) was investigated by Bahanurddin et al. (2015b) via high energy planetary ball mill to enhance the piezoelectric properties by avoiding evaporation of PO from the ceramic at elevated sintering temperature. The material exhibits high dielectric constant (ε_r = 5360). However, its piezoelectric properties (k_p and d_{33}) were not mentioned and the sintering temperature was not much lower. The volatilization of PbO from the ceramic during thermal treatment is another major issue which associated with the PZT (Kong et al., 2002). The loss of PbO fluctuate the electrical, optical and mechanical properties of the PZT ceramics (Garg et al., 1999; Song et al., 1989).

To overcome both the issues i.e. optimizing the k_p value and avoid the PbO loss of PZT ceramic for piezoelectric fan application. The dopant should be added which enhance the piezoelectric properties especially (k_p and ε_r) and reduces the sintering temperature without deteriorated the properties. Recently, k_p was enhanced by incorporating Li_2CO_3 in PZT system at low sintering temperature by many researchers (Hou et al., 2007; Vuong and Gio, 2013; Zeng et al., 2013; Fan et al., 2014). The increment in the k_p with other piezoelectric properties was due to the incorporation of Li^+ into crystal lattice. The Li^+ ions tend to occupy the octahedral sites of the lattice, which leads to the formation of additional anionic vacancies. The formation of these vacancies results in lattice distortion by lengthened the c-axis. Hence, Li_2CO_3 is appropriate candidate to enhance the k_p of the PZT material. Furthermore, it acts as a sintering aid (Wang et al., 1992). Due to its low melting point of Li_2CO_3 (723 °C) the liquid phase form which cover and wet the grains and therefore, improves the densification of the material at low sintering temperature. In later stage it reabsorbs into the lattice and modifies the properties. In the present work, PZT material which was previously doped with La^{3+} and Sr^{2+} is further doped with Li^+. The material is synthesized via high energy planetary ball milling to avoid PbO lost. Therefore, it is believed that the incorporation of Li^+ in PLSZT ($Pb_{0.93}La_{0.02}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$) system coupled with synthesized using high energy planetary ball milling could further enhance its piezoelectric properties especially k_p.

1.3 Objectives of the Research

The objectives of this research are:

- To synthesize PLSZT (PZT doped with La^{3+} and Sr^{2+}) and determine its dielectric and piezoelectric properties.
- To synthesize PLSZLiT (PLSZT doped with Li_2CO_3) at low temperature via high energy planetary ball milling.
- To determine the effect of Li_2CO_3 on the piezoelectric and dielectric properties of the PLSZT.

1.4 Thesis Structure

The work described in this thesis is organized into five chapters. Chapter 1 gives an overview of the ceramics and especially on the piezoelectric properties of the PZT electroceramic. In addition the affect of dopants and processing route on the piezoelectric properties of the PZT material are outlined. Finally, the problem associated with the piezoelectric and dielectric properties of the material, which required for thermal management of portable electronic devices by piezoelectric fan and the objectives of this study are presented.

Chapter 2 reviews the history of piezoelectricity and ferroelectricity. In addition the piezoelectric properties to measure the piezoelectric effect in the ferroelectric material are discussed. The previous work in La^{3+}, Sr^{2+} and Li^{+} doped and undoped PZT is reviewed. The effects of dopants on the piezoelectric properties of the PZT material are discussed in details. In addition, the approaches that adopted to densify the PZT material at low sintering temperature are also including in this chapter.

Chapter 3 describes the processing route and other steps, which is adopted to synthesize the doped and undoped PZT. Furthermore, different characterization techniques which were used for the analysis of the synthesized material are also present in this chapter. Finally, the sample preparation, equipments and the methods that were used to measure the piezoelectric properties such as ε_r, tan δ, d_{33}, K_P, and mechanical quality factor are discussed in this chapter.