EFFECT OF Ca ADDITION ON PIEZOELECTRIC AND DIELECTRIC PROPERTIES IN $Pb_{0.93}La_{0.02}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$ (PLSZT) SYSTEM

by

TUAN NUR IZZAH BINTI TUAN AB RASHID

Thesis submitted in fulfilment of the requirements for the degree of Master of Science

April 2018

ACKNOWLEDGEMENT

Alhamdulillah, praised to Allah The Almighty. This thesis would never have been completed without His guidance. First and foremost I would like to take this opportunity to thanks School of Materials and Mineral Resources Engineering (SMMRE) and the Dean of SMMRE, Prof. Dr. Zuhailawati Binti Hussain due to her generosity to let me experience how research life goes on. I also would like to express my special thanks of gratitude to my supervisor Assoc. Prof. Dr. Hasmaliza Mohamad, my co-supervisor Prof. Dr. Zainal Arifin Ahmad and Assoc. Prof. Dr. Ir. Julie Juliewatty Mohamed for their continuous supervision, guidance and support from the initial to the final stage of my research work.

My gratitude extents to Ministry of Education for part of research financial support under FRGS grant 6071282 for Grain Growth Control Mechanism of Lead Zirconate Titanate Electroceramic by doping La^{3+} and Sr^{2+}. Great thanks to the technicians of SMMRE, Mr. Sharul Ami Zainal Abidin, Mr. Kemuridan Md Desa, Mr. Mohamad Syafiq Abdul Majid, Mr. Abdul Rashid Selamat, Mr. Khairi Khalid and Mr. Zaini Saari for technical help. Besides, my deepest thanks to Prof. Dr. Mohammad Hafizuddin Jumali and Mr. Nizam in School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia for their helps during my research work, as well as my postgraduate members for moral support.

Last but not least, I am greatly indebted to my beloved parents Mr. Tuan Ab Rashid Tuan Mat and Mdm. Hasnah Mat for their patience pray, constant support and encouragement gives the warmth and strength to me. A lot of love for my siblings; Ms. Tuan Nur Izzati, Mr. Tuan Nur Izzat Syazwan and Mr. Tuan Nur Izzat Syazlan for their unconditional love motivates me to complete my work.

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LIST OF ABBREVATIONS

PZT	Lead zirconate titanate
PLSZT	Lead lanthanum strontium zirconate titanate
PCLSZT	Lead calcium lanthanum strontium zirconate titanate
Pb	Lead
Zr	Zirconium
Ti	Titanium
La	Lanthanum
Sr	Strontium
Ca	Calcium
MPB	Morphotropic phase boundary
XRD	X-ray diffraction
FESEM	Field emission scanning electron microscopy
DOE	Design of experiment
RSM	Respond surface methodology
rpm	Revolution per minutes

LIST OF SYMBOLS

λ	Wavelength
d_{33}	Piezoelectric coefficient
k_p	Electromechanical coupling factor
ε_r	Dielectric permittivity
$\tan \delta$	Dielectric loss
T_m	Melting temperature
T	Temperature
E_f	Electric field
t	Time
M_d	Weight of dry pellet
M_s	Weight of suspended pellet
M_w	Weight of saturated pellet
wt %	Weight percent
mol %	Concentration percent

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

ABSTRAK

Plumbum zirkonat titanat (PZT) adalah bahan piezoelektrik yang paling banyak digunakan di kalangan seramik. Gabungan La^{3+} dan Sr^{2+} terdop PZT (PLSZT) menunjukkan peningkatan dalam sifat-sifat piezoelektrik dan dielektrik iaitu pemalar piezoelektrik (d_{33}), faktor pengganding elektromekanik (k_p) dan pemalar dielektrik (ε_r). Walau bagaimanapun, d_{33} dan k_p masih lagi menunjukkan bacaan yang rendah untuk aplikasi peranti elektronik. Untuk meningkatkan d_{33} and k_p, proses pendopan dan pengkutuban telah dikaji. Dalam kajian ini, seramik $Pb_{0.93}La_{0.02}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$ (PLSZT) telah disintesis menggunakan pengisar bebola planet berkuasa tinggi selama 40 jam dan disinter pada suhu 1200 °C selama 3 jam. Parameter pengkutuban (suhu, medan elektrik dan masa) telah dikaji berdasarkan reka bentuk eksperimen (RBE) untuk mengkaji kesan parameter pengkutuban ke atas sifat-sifat piezoelektrik dan dielektrik bagi PLSZT. Selain itu, satu dopan baru ($CaCO_3$) bagi PLSZT telah dikaji diikuti dengan parameter pensinterannya (1100 °C hingga 1300 °C selama 2 hingga 4 jam) untuk meningkatkan lagi sifat-sifat piezoelektrik dan dielektrik. Parameter pengkutuban yang optimum telah menunjukkan bacaan d_{33} dan ε_r yang baik dan masing-masing adalah 320 pC/N dan 1660. Parameter pengkutuban yang optimum adalah pada T = 140 °C, E_f = 4 kV/mm dan t = 20 min. Ca^{2+} terdop PLSZT (PCLSZT) menunjukkan berlakunya peningkatan d_{33}, k_p dan ε_r pada penambahan Ca yang lebih rendah. Sifat-sifat piezoelektrik dan dielektrik yang optimum diperolehi pada 0.005 mol% Ca (PCLSZT0.005) yang disinter pada suhu 1200 °C selama 3 jam dengan d_{33} = 430

pC/N, k_p = 0.5866, ε_r = 2450 dan tan δ = 0.0426. Kesimpulannya, penambahan Ca^{2+} telah berjaya meningkatkan sifat-sifat piezoelektrik dan dielektrik PLSZT.

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ABSTRACT

Lead zirconate titanate (PZT) is a piezoelectric material which is most widely used in ceramics. La^{3+} and Sr^{2+} co-doped PZT (PLSZT) shows the improvement in piezoelectric and dielectric properties which were piezoelectric coefficient (d_{33}), electromechanical coupling factor (k_p) and dielectric permittivity (ε_r). However, the d_{33} and k_p still indicated a lower value for electronic device applications. In order to improve d_{33} and k_p, the doping process and poling behaviour were investigated. In this research, $Pb_{0.93}La_{0.02}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$ (PLSZT) ceramic was synthesized by high energy planetary ball milling for 40 hours and sintered at 1200 °C for 3 hours. The poling parameters (temperature, electric field and time) were studied based on design of experiment (DOE) in order to investigate the effect of poling parameter towards the piezoelectric and dielectric properties for PLSZT. Besides, a new dopant ($CaCO_3$) for PLSZT was studied followed by sintering parameters (1100 °C to 1300 °C for 2 to 4 hours) for further improving their piezoelectric and dielectric properties. The optimum poling parameter shows a good d_{33} and ε_r which were 320 pC/N and 1660, respectively. Poling parameters were optimized at T = 140 °C, E_f = 4 kV/mm and t = 20 min. Ca^{2+} doped PLSZT (PCLSZT) show that enhancement of d_{33}, k_p and ε_r occurred at lower Ca addition. Optimum piezoelectric and dielectric properties were obtained at 0.005 mol% $CaCO_3$ (PCLSZT0.005) sintered at 1200 °C for 3 hours with d_{33} = 430 pC/N, k_p = 0.5866, ε_r = 2450 and tan δ = 0.0426. In conclusion the addition of Ca^{2+} successfully increased the piezoelectric and dielectric properties of PLSZT.

CHAPTER ONE

INTRODUCTION

1.1 Piezoelectric material

Advance ceramics have provided greater control over aspects of composition and microstructure that govern physical properties. Such control makes it possible to tailor ceramics to fulfill special chemical, thermal, mechanical, and electrical requirements no other material can satisfy. Indeed, advanced ceramics have played critical roles in the development of new technology such as computers and telecommunications and they will continue to play a leading role in the technologies of the future. Their properties can be tailored to operation as insulators, ferroelectric materials, highly conductive ceramics, electrodes as well as sensors and actuators (Miclea et al., 2002; Shindo and Narita, 2012).

The piezoelectric material is a material that can create electricity when subjected to a mechanical stress also known as direct piezoelectric effect. They will also work in reverse, which is generating a strain by the application of an electric field and is known as indirect piezoelectric effect (Jordan and Ounaies, 2001). These electroceramics do not produce high piezoelectric behaviour due to the fact that the ceramics have a structure that consists of random orientations of grain. Therefore, these materials exhibit a polarized electrostatic effect where the electricity is applied in static material in order to rearrange the domain orientation in the grain. Thus, the ceramic must be polarized to align the orientation of the grain structures. The most commonly known piezoelectric materials are lead zirconate titanate (PZT) and barium titanate ($BaTiO_3$). Lead zirconate titanate is considered one of the most economical piezoelectric element, hence it is used in a lot of applications. As for the second one, barium titanate, it is a piezoelectric ceramic which is usually replaced by lead zirconate titanate for piezoelectricity (Frantti and Fujioka, 2011).

Piezoelectric ceramics, usually based on lead zirconate titanate (PZT) which is an intermetallic inorganic compound with the chemical formula $Pb(Zr_xTi_{1-x})O_3$ ($0 \leq x \leq 1$). PZT is a ceramic perovskite material that shows a marked piezoelectric effect, meaning that the compound is used in a number of practical applications in the area of electroceramics such as sonars, ultrasonic cleaners, buzzers, accelerometers, ultrasonic motors and piezo transformers (Carter and Norton, 2007). Piezoelectric ceramics based on PZT are widely used for numerous applications in the microelectronics industry. In order to tailor the physical properties required in specific applications, PZT ceramics were usually doped with small amounts of other oxides. The compositions nearing the morphotropic phase boundary (MPB) exhibit a good piezoelectric activity. MPB exhibits good piezoelectric properties because the boundary consists of two phases (tetragonal and rhombohedral) which can enhance domain wall mobility and facilitate polarization rotation. Thus, improve the dielectric and piezoelectric properties. Therefore the Zr/Ti ratio in the ceramic has also been given an important consideration in the production of PZT ceramics. This is because the MPB is exists in between the ratio of Zr/Ti in the phase diagram. The effects of Zr/Ti ratio and those of different additives such as Mn, Sr, La and others on the structural and electrical properties of PZT ceramics were investigated extensively in various earlier studies (Nogas-Cwikiel, 2011; Devi et al., 2012; Nguyen et al., 2014).

The perovskite structure is originally cubic with A^{2+} ion at the edge, B^{4+} ion at the centre and O^{2-} ion at the center face position, representing the cell. In order to improve dielectric, piezoelectric and mechanical properties, the PZT ceramics with perovskite structure (ABO_3) are usually substituted in A-sites or/and B-sites. The major reasons for these improvement were due to the presence of cation vacancies during donor doped (soft dopant) while presence of oxygen vacancies in acceptor doped (hard dopant) (Frayssignes et al., 2004). Typically, soft dopant ceramics such as La, Nd, Sr, Sb, Bi, Ca and other rare earth always possess high permittivity and electromechanical coupling factor, which suitably serve as receiver type transducers, sensor and actuator application. The additives such as Nb_2O_5 and CaO are known as soft dopant because they decrease the coercive field and elastic modulus. Meanwhile, hard dopant ceramics such as K, Na, Fe and Mn are used as emission type transducer due to their high tensile strength and mechanical quality factor, as well as low loss (Yu et al., 2015). Hard dopant PZT can also withstand high electrical excitation which is suitable for high power application. Meanwhile, the additive of Fe_2O_3 and MnO_2 act as hard dopant because they increase the coercive field and elastic modulus (Ibrahim et al., 2003).

Many investigations have been done on altering the composition of the piezoelectric materials. The composition of PZT system has been altered with various dopants in order to improve electrical properties for high technology applications. Aside from altering the composition, the parameters of poling process (polarization) also contributed towards the electrical and mechanical properties of the system especially in dielectric and piezoelectric properties (Cavalcante et al., 2006; Kalem and Timucin, 2013; Kainz et al., 2016). In poling process, electric field and temperature have a significant effect on improving the electrical properties. Li et al. (2011), generally believed that temperature plays an important role during the poling process because it leads to the optimization of the piezoelectric properties. This is because during poling process the sufficient high electric field is applied to the ceramic sample, the domains undergo orientation and align the domains in the allowable directions closest to the direction of applied field. After the removal of electric field, the orientation of domains is partially retained and ceramic exhibits the piezoelectric effect (Kholkin et al., 1998). Several researchers studied the effect of poling towards the properties of PZT ceramics especially in dielectric and piezoelectric properties. They claimed that the poling temperature and electric field strongly influence the conversion between electrical and mechanical energy (Jaitanong and Chaipanich, 2008; Prewitt and Jones, 2011; Yu et al., 2015).

PZT is widely used in cooling application such as actuators and sensors. The most commonly piezoelectric actuators is known as piezoelectric fan (Liu and Liaw, 2004). Previously, the conventional cooling system such as rotary fan and heat sink were used for thermal management of portable electronics devices. However, the piezoelectric fans are moving towards supplementing the cooling of stagnant areas and hot spots where the cooling of the rotational fan is less effective (Acikalin et al., 2004). Piezoelectric fans are capable of enhancing electric machine housing heat transfer and have been used in a number of applications, mainly in electronics cooling. However, their application to electrical machine cooling has not been previously considered and became a challenge (Gilson et al., 2013).

1.2 Problem Statement

The use of PZT ceramic system in industry has gained attention among researchers due to the good performance in piezoelectric properties. Even though many researchers studied about the lead-free piezoelectric materials due to toxicity, PZT systems still give the best performance especially in piezoelectric properties. PZT materials are well known in electronic applications for their good piezoelectric properties and are ideal candidates for making sensors and actuators (Ramana et al., 2010). PZT is always modified with dopants for further improvising the electrical properties such as piezoelectric permittivity (d_{33}), electromechanical coupling factor (k_p) and dielectric permittivity (ε_r) that is required for specific applications. Therefore, various researchers have studied about the substitution of ions from dopant materials (Sr, Mn, Nb, La, Fe and other rare earth metals) in order to improve the densification and to enhance the dielectric and piezoelectric properties (Wu et al., 2013; Aleem et al., 2013; Bahanurddin et al., 2015; Kour et al., 2014).

Among the dopants, the behaviour of La^{3+} doping in PZT system shows an increment in aspects of the piezoelectric, dielectric and ferroelectric. However, the incorporation of La^{3+} in the PZT system profound effects on dielectric properties due to the growth inhibitions and caused of degradation of k_p (Pdungsap et al., 2005; Sahoo and Panda, 2013). They reported that the excess of La^{2+} was precipitated in the grain boundary and slowed the grain growth hence reduces the electrical properties. Another research was studied with co-doped two dopants material in the PZT system which were La^{3+} and Sr^{2+} in order to enhance its properties (Kalem et al., 2011). However, they found that when a higher composition of La^{3+} is used, the k_p was decreased due to growth inhibition. Meanwhile, Devi et al. (2012) claimed that the introduction of Sr^{2+} in lead lanthanum zirconate titanate (PLZT) decreased the dielectric permittivity and exhibited a maximum value of ε_r = 1523. The decrease in the dielectric permittivity attributed partly to the increase of the compositional heterogeneity produced by a greater atomic diffusion and presence of lead vacancies.

Bahanurddin et al. (2015) also studied on La^{3+} and Sr^{2+} co-doped PZT via high energy planetary ball mill and shows good dielectric properties (dielectric permittivity was 5360) but the piezoelectric properties were not mentioned. Moreover, Siddiqui et al. (2017) profound effects of Li^{+} on PLSZT but the d_{33} value was decreased from 315 pC/N to 259 pC/N. However, the d_{33} and k_p was still indicated as a lower value for electronic device applications. According to Yorinaga et al. (1985), the higher d_{33} (>350 pC/N), k_p (>0.5) and ε_r are desirable for application of the electromechanical devices such as piezoelectric fan. High d_{33} and k_p in poled PZT ceramics are believed to arise from the motion of domain walls under the action of applied field or stress.

Apart from the doping process, the poling behaviour also plays an important role in obtaining better dielectric and piezoelectric properties. A few studies have been reported on poling parameters where referred to electric field, temperature and time taken for poling process (Li et al., 2011; Yu et al., 2015). Prewitt and Jones (2011) reported that temperature was the most influenced parameter in poling process due to domain wall motion was thermally activated at an elevated temperature. This would promote a higher degree of domain orientation, which leads to a larger developed polarization, and thus, increases the piezoelectric coefficients. However, the influences of poling parameter on piezoelectric coefficient are focusing only on undoped PZT system and no details studies on doped PZT.

Therefore, in this case, the poling behaviour of La^{3+} and Sr^{2+} co-doped PZT (PLSZT) was further investigated using Design of Experiment (DOE) concept to understand the poling parameter effects on the dielectric and piezoelectric properties. DOE was used to ensure the research or experiment in generating a valid, defensible, and supportable conclusions. Besides, a new dopant ($CaCO_3$) doped in PLSZT was also investigated to improve the electrical properties in PLSZT system. A Ca^{2+} ion proved that it would promote a polarization of the unit cell which results in increasing of remnant polarization. Thus, enhancing the dielectric and piezoelectric properties (Mohiddon and Yadav, 2008; Kour et al., 2014; Silva et al., 2015). Lead