SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

EFFECT OF CALCIUM CONCENTRATION ON THE MICROSTRUCTURE AND DIELECTRIC PROPERTIES OF CA-DOPED PLSZT (Pb-La-Sr-Zr-Ti) SYSTEM

By

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Dissertation submitted in partial fulfillment
of the requirements for the degree of Bachelor of Engineering with Honours
(Materials Engineering)

Universiti Sains Malaysia

JUNE 2017

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Effect of Calcium Concentration on the Microstructure and Dielectric Properties of Ca-doped PLSZT (Pb-La-Sr-Zr-Ti) System**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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AKNOWLEDGEMENTS

First of all, I would like to thank School of Materials and Mineral Resources University Sains Malaysia and Dean of the school, Prof. Dr. Zuhailawati binti Hussain. It is an opportunity that allows students to apply what they had learned in their academic study for the past few years. It also gave me the chance to sharpen my thinking and gain knowledge as well as practical skill that will be useful in the future.

I also would like to thanks my supervisor, Assoc. Prof. Dr. Hasmaliza Mohamad, who always gave encouragement, guidance and support from the initial to the final stage of the research. She gave me useful advice throughout the whole final year project and helped me identify my weaknesses in which i had managed to overcome.

Besides that, I would like to thank Tuan Nur Izzah, one of the master students of Assoc. Prof. Dr. Hasmaliza Mohamad who helped and guided me a lot to carry out the experiment. She had guided me in sample preparation, synthesis and characterization of samples. I also would like to deliver my thanks to all the technicians, especially Mr. Kemuridan, Mr.Mohamad Shafiq, Mr. Abdul Rashid, Mr. Mohamad Zaini, Mr. Muhammad Khairi and Mr. Shahrul for always helped me in the project. .

Lastly, I would like to thank all my family and my friends who always support me for the completion of my final year project. Thank you very much.

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ABSTRAK

Plumbum zirkonat titanat (PZT) mempunyai struktur perovskite dan sifat piezoelektrik yang tinggi. Sifat dielektrik PZT dapat dipertingkatkan dengan penambahan dopan. Dalam penyelidikan ini, kesan pelbagai kepekatan kalsium terhadap mikrostruktur dan sifar-sifat dielektrik bagi PLSZT (Pb-La-Sr-Zr-Ti) terdop kalsium telah dikaji. Serbuk bahan mula yang berketulinan tinggi ditimbangkan mengikut formula molekul $Pb_{0.93-x}Ca_xLa_{0.02}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$ dengan x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10. PLSZT terdop kalsium dihasilkan dengan munggunakan kaedah tindak balas bebola pengisar berkelajuan tinggi dan dibakar pada 1200 ºC selama 3 jam dengan kadar pemanasan 5 ºC setiap minit. Pencirian sampel-sampel telah dijalankan dengan menggunakan XDR, SEM dan LCR meter yang bermula dari 1 kHz kepada 1 MHz. Keputusan XRD menunjukkan semua sampel PLSZT terdop kalsium mempunyai fasa tetragonal dan rombohedra dan SEM menunjukkan saiz butiran sampel menjadi kecil dengan peningkatan kepekatan kalsium. Walau bagaimanapun, saiz butiran mula membesar pada 8 mol% (x = 0.08) kalsium. Ketumpatan pula menurun dengan kenaikan kepekatan kalsium. Pemalar dielektrik dan kehilangan dielektrik sampel menurun dengan peningkatan frekuensi voltan dari 1 kHz kepada 1MHz. pemalar dielektrik meningkat dengan kepekatan kalsium. Antara kesemua komposisi yang dikaji, sampel seramik PLSZT terdop 10 mol% (x = 0.10) kalsium menunjukkan pemalar dielektrik yang tinggi.

EFFECT OF CALCIUM CONCENTRATION ON THE MICROSTRUCTURE AND DIELECTRIC PROPERTIES OF CALCIUM-DOPED PLSZT (Pb-La-Sr-Zr-Ti) SYSTEM

ABSTRACT

Lead zirconate titanate (PZT) has perovskite structure and exhibits strong piezoelectric properties. PZT is recently modified by adding dopants to improve the dielectric properties. In this study, the effect of various calcium concentrations on the microstructure and dielectric properties of Ca-doped PLSZT (Pb-La-Sr-Zr-Ti) is investigated. The starting high purity powder is weighed according to the molecular formula $Pb_{0.93-x}Ca_xLa_{0.02}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$ with x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10. Ca-doped PLSZT was prepared using high planetary ball mill, palletized and sintered at 1200 ºC for 3 hours with heating rate 5 ºC per minute. Characterizations of the samples were carried out by using XRD, SEM and LCR meter which measured from 1 kHz to 1 MHz. XRD results showed that all Ca-doped PLSZT samples present tetragonal and rhombohedral phase whereas SEM results showed that the grain size of the samples was decreased with increasing calcium concentration. However, the grain size began to enlarge at 8 mol% (x = 0.08) of calcium. The density was observed to be decreased with increasing amount of calcium. The dielectric constants and dielectric loss of samples were decreased with the increasing frequency of applied voltage from 1 kHz to 1 MHz. The dielectric constant is increased with the concentration of calcium. Among all the compositions studied, 10 mol% (x = 0.10) of Ca-doped PLSZT ceramic sample showed remarkable dielectric constant.

CHAPTER 1

INTRODUCTION

1.1 Piezoelectric Materials

Piezoelectric material is a material in which when it is loaded with a pressure, it is compressed as any other elastic material and extended transversal to the direction of the load. The material will undergo deformation and polarization phenomenon will be occurred in the interior of material. Electrical charges will be generated and accumulated in response to the applied mechanical stress. The piezoelectric effect is a reversible process in that the direct piezoelectric effect (generation of electrical charge under a n applied mechanical strain) can be reserved to generate a mechanical strain via the application of an electrical charge (reverse piezoelectric effect) (Horrocks and Anand, 2016).

Piezoelectric materials can be classified into monocrystalline materials and ferroelectric materials. Monocrystalline materials, for example, quartz, zinc oxide, and lithium niobate whereas ferroelectric materials, for example, ceramics lead zirconate titanate (PZT) and barium titanate ($BaTiO_s$) are very well known to be used as dielectric materials for multilayer ceramic capacitors, electronic and optoelectronic devices (Schomburg, 2011).

1.2 Lead Zirconate Titanate (PZT)

Lead zirconate titanate (PZT) is a solid solution of two materials (i) a ferroelectric lead titanate ($PbTiO_3$), and (ii) an anti-ferroelectric lead zirconate ($PbZrO_3$) (Panda & Sahoo, 2015). Ferroelectric materials exhibit a spontaneous electric polarization, whose direction can be switched by an applied electric field. Upon cooling from sintering temperature, ferroelectric ceramics undergo a phase transition from paraelectric to a ferroelectric state, and is observed at the curie temperature. This leads to the formation of domains. These domains can be reoriented by poling and results in a remnant polarization as well as dimensional changes of the ceramics. PZT exhibits a strong piezoelectric response for compositions around morphotropic phase boundary (MPB) because of the diverging piezoelectric coefficients (Erhart and Albe, 2015). Piezoceramics is of intense interest and technological important in many applications, such as microelectronics through positioning elements in photolithography, medical diagnostics through ultrasound imaging, sensors and actuators in automobile industry, and many others (Rodel et al.,2015).

The properties of PZT ceramics can be modified for specific applications by adding dopants, such as donor and acceptor doping, isovalent substitutions and addition of low melting additives (Galassi et al., 2012). Donors, for example, replacing Zr^{4+} with Nb^{5+} or replacing Pb^{2+} with La^{3+}. The addition of these dopants is usually compensated to maintain electroneutrality by the formation of Pb^{2+} vacancies. Donors enhance domain reorientation, and materials produced with these additives are characterized by rectangular hysteresis loops, low E_c, high P_r, high κ, maximum k, high $\tan\delta$, high elastic compliance, and reduced aging. Typical applications are in areas in which high sensitivity is required, such as hydrophones, sounders, and loudspeakers.

However, acceptors such as Fe^{3+} replaced Zr^{4+} with the concomitant formation of oxygen vacancies. Domain orientation is limited, and hence acceptor additives lead to poorly developed hysteresis loops, lower κ, low tanδ, low compliance, and high aging rates. Typical applications are in high-power devices such as sonar and ultrasonic transducers (Carter and Norton, 2007). Isovalent dopants with ions of the same valence and similar size, such as Ba^{2+} or Sr^{2+} for A sites or Sn^{4+} for B sites, tend to inhibit domain reorientation and reduce the Curie temperature (Galassi et al., 2012).

1.3 Problem Statement

In previous research, Kalem et al. (2011) have reported that addition of Sr and La as co-dopants into PZT ceramics stabilized the tetragonal phase. The incorporation of Sr^{2+} into the PZT lattice enhanced the grain growth during sintering while La tended to decrease the grain size. The satisfactory densification is achieved due to effective development of microstructure consisting of large and small grains. Besides, addition of Sr and La had intense implications on the dielectric and piezoelectric properties of PZT ceramics. A high piezoelectric strain coefficient d_{33} of 640pC/N was also attained in the PLSZT ceramic containing 1 at% La and 5 at% Sr. Kalem and Timucin (2013) worked on PLSZT system which exhibited high piezoelectric strain coefficient d_{33} by co-doping with manganese and niobium, which were introduced to the “B” site of the PSLZT. The researchers claimed that the grain size decreased and curie temperature of PSLZT-PMnN ceramics decreased gradually with the increasing of manganese and niobium addition.

Bahanurddin et al. (2015) doped PZT with La^{3+} and Sr^{2+} via high energy planetary ball mill process. They found that the evaporation of PbO during calcination and sintering processes can be avoided by virtue of its ability to skip the calcinations step. However, the sintering of the PZT ceramic was carried out at high temperature of 1150 °C, which was slightly lower than the usual sintering temperature for the PZT ceramic. The ceramic was found to exhibit high dielectric constant, $\varepsilon r=5360$ but their k_p and d_{33} values were not mentioned.

In order to optimize k_p of the PZT ceramics, Siddiqui et al. (2017) doped $Pb_{0.93}La_{0.02}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$ (PLSZT) ceramics with Li^+ and was synthesized via high energy planetary ball milling. It is found that Li_2CO_3 addition able to improve the densification and increase the average grain size. The piezoelectric and dielectric properties were found to be enhanced with the increase in Li^+ content.

On the other hand, Kour et al. (2014) studied the effect on the electrical properties of calcium modified PZT, $Pb_{1-x}Ca_xZr_{0.52}Ti_{0.48}O_3$ with x = 0.00, 0.02, 0.04, 0.06 and 0.10 composition. From the study, it revealed that the grain size of Ca-doped PZT decreased with the increase in calcium concentration due to small ionic radius of calcium as compared to the ionic radius of lead. Whereas dielectric constant increased with increase in calcium concentration as results of increase in lattice distortion due to ionic radius mismatch, and local distortion in Pb site.

Hence, in this research, calcium is doped to the “A” site of $Pb_{0.93}La_{0.02}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$ (PLSZT) with x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10 to enhance its electromechanical properties. The influence of calcium concentration on the microstructure and dielectric properties of Ca-doped PLSZT were studied.

1.4 Objectives

a) To study on the fabrication of Ca-doped PLSZT

b) To investigate the effect of various calcium concentration on the microstructure and dielectric properties of Ca-doped PLSZT

1.5 Scope of Research

In this work, PLSZT will be doped with calcium with concentration of calcium, x= 0.02, 0.04, 0.06, 0.08 and 0.10. Undoped and Ca-doped PLSZT will be synthesized using high energy planetary ball mill. Various characterizations include X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Energy-dispersive X-ray Spectroscopy (EDX) will be used in this study. Besides, the densities of the sample will be measured based on Archimedes principal while dielectric constant will be carried out by measurement of dielectric constant and dielectric loss on the impedance analyzer.

The raw materials are in the form of high purity powder which are PbO, ZrO_2, TiO_2, La_2O_3, $SrCO_3$ and $CaCO_3$. At the beginning of the study, raw powders will be characterized using XRD, SEM and EDX. The same characterization techniques will be used for the sintered pellets at 1200°C. The measurement of dielectric constant and density will be tested on the sintered pellet.

1.6 Flow Chart of Overall Process

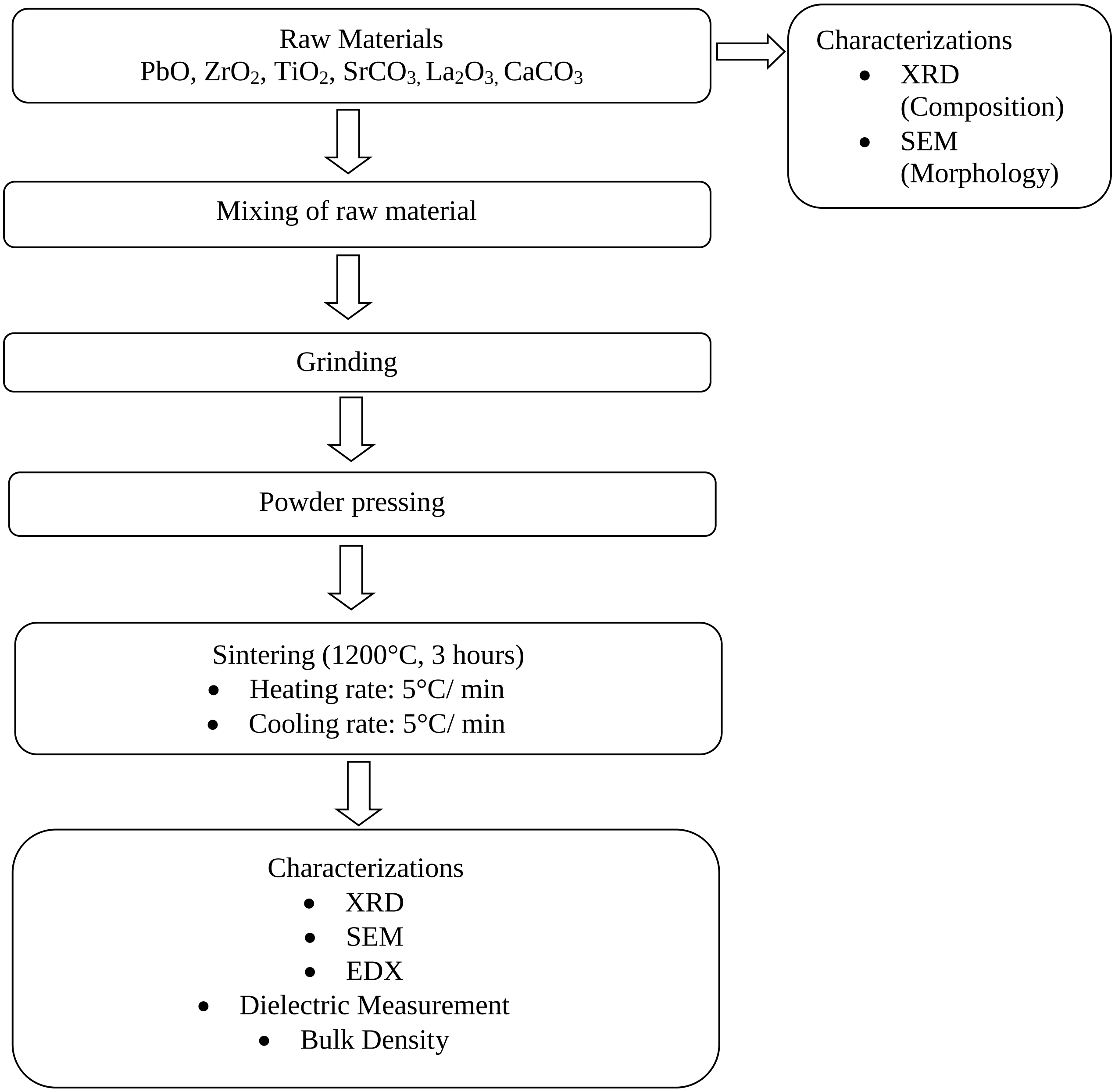


Figure 1.1: Overall flow chart of the study

CHAPTER 2

LITERATURE REVIEW

2.1 Ceramics

Ceramics are both man-made and manufactured inorganic non-metallic solid materials which have been shaped and fired in a high temperature. The name “ceramic” comes from “keramos”, with the meaning of clay used by potters and object made of clay, which originated from “keramikos” in Greek (Japan, 2012). In its modern context, ceramics contain an extremely broad range of inorganic materials which can be divided into non-metallic and metallic elements. They have wide variety of manufacturing techniques which can be used to produce ceramics. Traditionally, ceramics are moulded from silicate minerals, such as clays, dried and fired at temperatures of 1200-1800°C to give a hard finish. Thus the original Greek word “keramos” represents ‘burned stuff’ or ‘kiln-fired material’ which has long been directly appropriate. However modern ceramics are usually made by the process which do not involve a kiln-firing step, for example hot pressing, glass devitrification and reaction-sintering. Ceramics are non-metallic in character which distinct from metals and alloys. They have become increasingly inadequate and arbitrary as new ceramics with unusual properties are developed and come into use (Smallman and Bishop, 1999).

Generally, ceramics are classified according to type or function in various ways. In industrial terms, they may be listed as pottery, refractories (fire-bricks, silica, alumina, basic, neutral), heavy clay products (bricks, earthenware pipes, etc.), concrete and cement, glasses and vitreous enamels and engineering (technical, fine) ceramics. Engineering ceramics, also known as advanced ceramics, are capable of very high strength and hardness, exceptional chemical stability and can be manufactured to very close dimensional tolerances. Engineering components has been introduced based on considerable scientific effort and has revolutionized engineering ceramics design practice (Smallman and Bishop, 1999).

In general, the advanced ceramics sector comprises of the following categories (Rödel et al., 2009):

i. Functional ceramics: Electrical and magnetic ceramics (i.e. dielectrics, piezoelectrics, ferromagnetics), ionic conductors and superconductive ceramics.
ii. Structural ceramics: Monoliths and composites, for example oxides, nitrides, carbides, borides, and composite materials based on these materials.
iii. Biomaterials: for example hydroxyapatite and alumina.
iv. Ceramic coatings: Oxides, nitrides, carbides, borides, cermets and diamond-like coatings, deposited by technologies such as spraying, vapour deposition and sol-gel coating.
v. Special glasses: Processed flat glass, fire resistant glazing and glasses for optoelectronics.

There has been great interest shown in high technology or advanced ceramic materials among scientists, policymakers and corporations. Varieties of ceramic materials, which hold remarkable properties and able to meet the need for high end applications, have appeared. The substitutions of advanced ceramic materials for traditional parts in many applications result in substantial productivity improvements and high performance (Liang and Dutta, 2001). The development of advanced ceramics has been stimulated by the drive towards higher, more energy-efficient process temperatures and foreseeable shortages of strategic minerals. In contrast to traditional ceramics, advanced ceramics depends upon the availability of purified and synthesized materials and upon close microstructural control during processing (Smallman and Bishop, 1999).

2.1.1 Electroceramics

Electroceramics are ceramics that feature electrical, electronic and magnetic properties. When there are slight differences in compositions and crystal structures of ceramics, its electrical and magnetic properties usually change substantially. On the other hand, if appropriate compositions and crystal structures are selected, almost all electromagnetic properties, such as insulation properties, electrical conductivity, semiconductive properties, magnetic properties and superconductive properties can be achieved (Japan, 2012).

Electroceramic materials have become increasingly important in key technologies such as computers, telecommunications and aerospace (Schwartz, 2006). They were primarily from the perspective of their insulating or dielectric properties. Applications such as high-voltage standoffs, capacitors, spark plugs and the like followed maturally. In recent decades, however, this picture of ceramics has changed rapidly. It has now become more evident that ceramics exhibit the full spectrum of electrical properties spanning the gap from superconducting to insulating electronic conductors and from fast ionic to insulating ionic conductors. In many cases, it is the unique combination of desired electrical properties together with the characteristic stability of ceramics that renders them the obvious choice for many technological applications (Buchanan, 2004).

The primary types of electroceramic materials include piezoelectric, pyroelectric, and ferroelectric materials, dielectric materials, electro-optic and electro-chromic materials, semiconductors, ionic conductors, mixed conductors, magnetic materials， superconductors, and photo-electrochemical materials (Schwartz, 2006). Example of electroceramics include zinc oxide for varistors, lead zirconium titanate (PZT) for piezoelectrics, barium titanate in capacitors, tin oxide as gas sensors, lead lanthanum zirconium titanate (PLZT) and lithium niobate for electro-optic devices (Segal, 1991).

2.2 Piezoelectric Materials

Piezoelectric material is a material in which when it is loaded with a pressure, it is compressed as any other elastic material and extended transversal to the direction of the load. The material will undergo deformation and polarization phenomenon will be occurred in the interior of material. Electrical charges will be generated on electrodes on the surface of the piezoelectric material and it is possible to measure voltage between the electrodes. The generation of charges is called the piezoelectric effect and the material is called a piezo. The word “piezo” is originated from Greek with the meaning of “I am pressing”. This piezoelectric effect is employed to measure strains, forces, or pressures. In addition, there is also an inverse piezoelectric effect. When a voltage is supplied to the electrodes, the piezoelectric material is straining both longitudinal and transversal to the electric field. This inverse piezoelectric effect is employed to build actuator (Schomburg, 2011).

There are two types of piezoelectric materials which are monocrystalline materials and ferroelectric materials. Monocrystalline materials include quartz, zinc oxide, and lithium niobate, whereas ferroelectric materials include ceramics lead zirconate titanate (PZT) and barium titanate ($BaTiO_s$) (Schomburg, 2011).

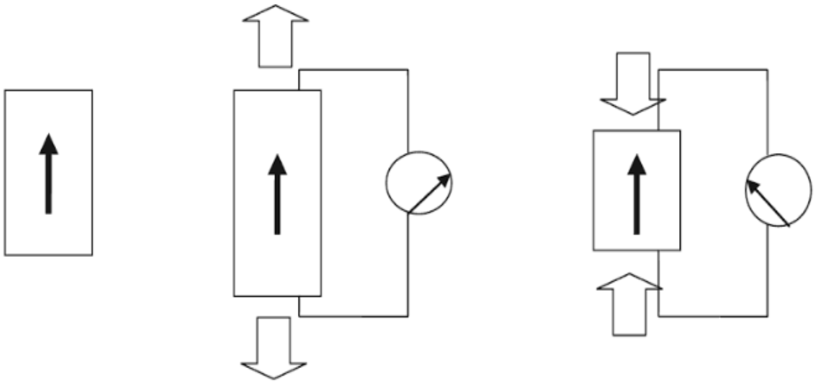
Quartz, which is a natural piezoelectric material, has been widely used for piezoelectric transducers and popular for pressure measurement due to its high piezoelectricity, high mechanical strength, high voltage sensitivity and high thermal resistance. However, its applications are often limited due to its vulnerability to high temperature and liquid. In order to overcome these limitations and improve the piezoelectric performance, PZT and $BaTiO_s$ become alternative materials for transducer manufacturing because they exhibit much higher piezoelectricy and piezoelectric voltage constants than quartz (Wang et al., 2014).

Piezoelectric ceramics also find useful applications as dielectric materials for multilayer ceramic capacitors, electronic and optoelectronic devices due to their high dielectric constant, low dielectric loss, and low cost. They are generally quite brittle and require high processing or sintering temperatures. In the energy storage technologies, dielectric capacitors possess an intrinsic high-power density due to their very fast energy uptake and delivery, and thus show great promise for making high-performance power electronics used in hybrid electric vehicles, medical devices, and electrical weapon systems (Tjong, 2013).

2.2.1 Piezoelectricity

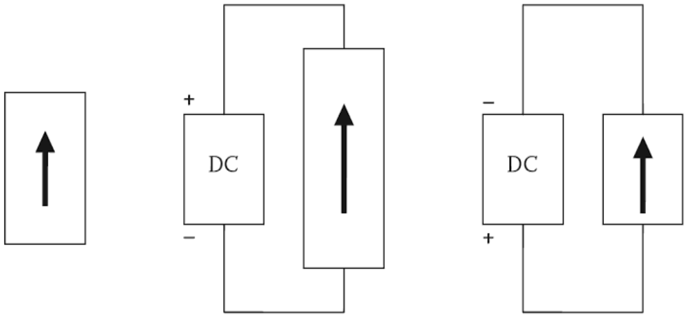
Piezoelectricity is the ability of certain crystalline materials to develop an electric charge proportional to a mechanical stress. This is called direct piezoelectric effect and was discovered by Jaques and Pierri Curie in 1880 (Jaffe, 2012). In other words, piezoelectric material changes its polarization under stress. Piezoelectricity is related to permanent polarization, and can be attributed to the permanent polarization being changed when the material undergoes mechanical deformation due to applied stress. Conversely, the change in permanent polarization produces a mechanical deformation, strain. This is called inverse piezoelectric effect (Giurgiutiu and Lyshevski, 2016).

In the direct piezoelectric effect (Figure 2.1), a positive voltage is generated across the faces when a poled piezoelectric material is subjected to tensile stress in the direction parallel to the poling direction. A negative voltage is generated across the faces when the material is subjected to compressive stress in the direction. However, in the inverse piezoelectric effect (Figure 2.2), when an external voltage is applied to the material, the material gets extended if the polarity of the voltage is the same as that of the field applied during poling. In the other hand, when the voltage is applied in the reverse direction, the material gets compressed (Vijaya, 2016).



(a) (b) (c)

Figure 2.1: Direct piezoelectric effect: (a) Poled piezoelectric material. (b) When tensile stress is applied to the material, the material develops voltage across its face with the same polarity as the poling voltage. (c) When a compressive stress is applied to the material, the material develops voltages with polarity opposite to that of the poling voltage (Vijaya, 2016)



(a) (b) (c)

Figure 2.2: Inverse piezoelectric effect: (a) Poled piezoelectric material. (b) When a DC field is applied with the same polarity as the poling field, the material develops tensile strain. (c) When a DC field is applied in the reverse direction, the material develops compressive strain (Vijaya, 2016)

The direct and the inverse piezoelectric effects have many applications due to the effects involve conversion of mechanical energy into electrical energy and vice-versa. The applications include generation and detection of ultrasonic waves, pressure sensors, and actuators. Ultrasonic is used in both engineering and medical fields. In engineering field, it is used in non-destructive testing of materials (NDT), underwater acoustics (SONAR), ultrasonic drilling, energy harvesting whereas in medical fields, it is used for diagnosis (sonography), therapy (drug delivery) and surgery (Vijaya, 2016).

2.3 Ferroelectric Materials

Ferroelectric materials can be categorized into four groups, these are perovskite group, pyrochlore group, tungsten-bronze group and bismuth layer structure group. Among these four groups, the most important group is the perovskite group. Perovskite group is expressed as ABO_3. A structural phase transition is occurred in most ferroelectric materials, in which the phase changes from a high temperature paraelectric phase into a low temperature ferroelectric phase. The temperature of this phase transition is known as Curie temperature (T_c). Different ferroelectric material will have their unique T_c value. The phase transition of ferroelectric leads to substantial anomalies in dielectric, elastic, thermal and other properties of the materials. The dielectric variation before and after a phase transition is the most significant and usually used as an indication of phase transition (Kong et al., 2008).

Barium titanate ($BaTiO_3$) is the first ferroelectric ceramic material and was discovered in the mid-1940s. Before the discovery of $BaTiO_3$, steatite, mica, TiO_2, $MgTiO_3$

and $CaTiO_3$, were the most widely used materials for capacitors with dielectric constant of $\leq$100. However, there was a demand for high dielectric constant materials to fabricate high capacitance capacitors during the World War II. $BaTiO_3$ has been studied as a high dielectric constant material and it was concluded that the source of its high dielectric constant is due to its ferroelectric properties (Haertling, 1999). In previous study, hydrothermal preparation of tetragonal-$BaTiO_3$ with nanometer-sized had excellent dielectric properties with high dielectric constant (~6900) and low dielectric loss (Xu and Gao, 2003).

Besides, the history of ferroelectric ceramics materials also include lead zirconate titanate (PZT) piezoelectric ceramics, lead lanthanum zirconate titanate (PLZT), lead magnesium niobate (PMN) relaxor ferroelectric ceramics and other non-perovskite ferroskite ceramics (Haertling, 1999).

PZT and PLZT have been used in transducer application. They possess higher electromechanical coupling coefficients and wide range of dielectric constants. Besides, they have higher T_c value which permit higher temperatures of operation or higher temperatures of processing during the fabrication of devices. They can be sintered easily at low temperature than $BaTiO_3$ and form solid-solution compositions with many different constituents, and thus allowing a broad range of achievable properties. Whereas PMN ceramic is one of triaxial components in the PZ-PT-PMN solid-solution system. The most popular specific composition in this system is PMN-PT, in which PMN containing 10% PT, thus increasing the temperature of maximum dielectric constant for relaxors (Haertling, 1999).

2.3.1 Properties of Ferroelectric materials

The useful properties of ferroelectric ceramics are related to their response with an electric field. The electrical behavior of these materials is significant to their successful application in dielectric, piezoelectric, pyroelectric, or electrooptic devices. Generally, ferroelectrics have the following electrical characteristic (Haertling, 1999) :

i. higher dielectric constants (200–10 000) than ordinary insulating substances (5–100), making them useful as capacitor and energy-storage materials,
ii. relatively low dielectric loss (0.1%–7%),
iii. high specific electrical resistivity (>1013 Vz cm),
iv. moderate dielectric breakdown (100–120 kV/cm for bulk and 500–800 kV/cm for thin films) and
v. nonlinear electrical, electromechanical, and electrooptic behavior.

Dielectric materials are ceramic materials with good electrical insulator. Although these materials do not conduct electric current during the application of electric field, they are not inert to the electric field. The electric field will cause a slight shift in the balance of charge within the material, and hence form an electrical dipole as shown in Figure 2.3 (Richerson et al., 2005).

The formation of an electrical dipole is called polarization. The term relative dielectric constant (*K'*), also known as relative permittivity, is defined the degree of polarizability or charge storage capability of a material. Capacitance is a measure of the charge storage capacity for a given potential difference.. The concept of the relative dielectric constant is illustrated in Figure 2.4. When an electric field is applied to two flat plates of a metal such that one plate becomes positive and the other negative, the electric field causes polarization in the material in the space between the conductive plates. The relative dielectric constant compares the polarizability or charge storage of the material with that of a vacuum between the plates (Richerson et al., 2005).

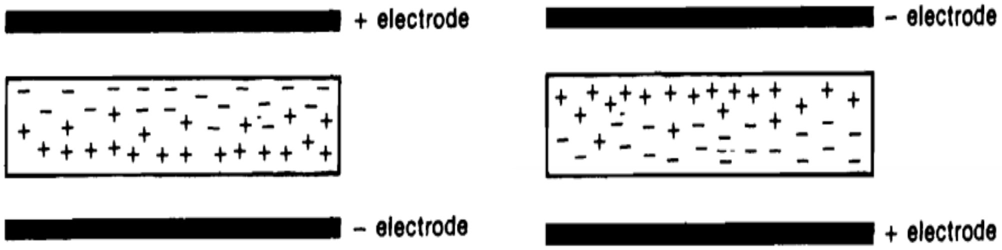


Figure 2.3: Shift in the distribution of charge in a ceramic insulator when it is placed in an electric field between two electrically conductive electrodes (Richerson et al., 2005)

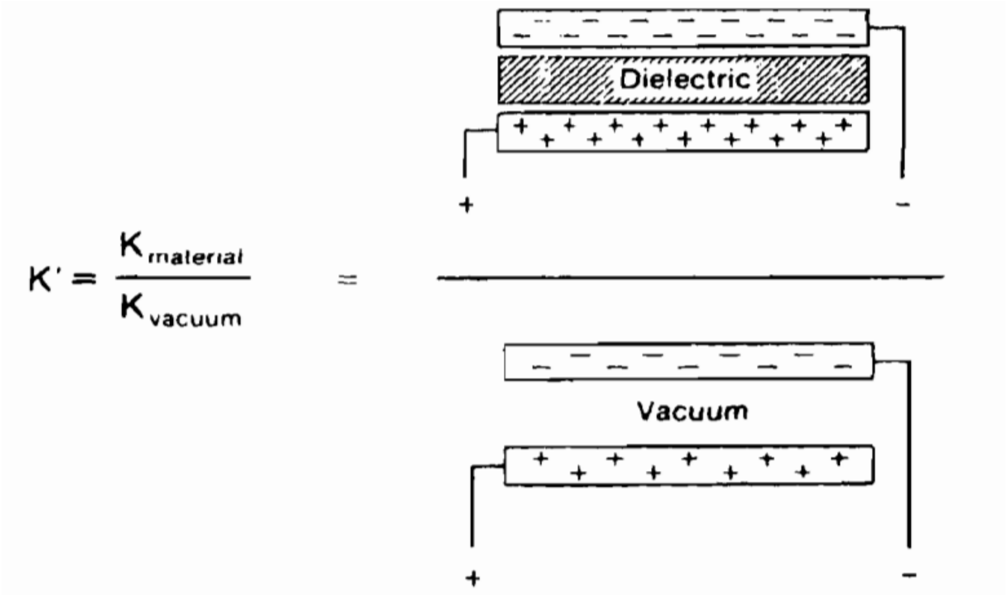


Figure 2.4: The definition of the relative dielectric constant, *K’* (Richerson et al., 2005)

The dielectric properties such as dielectric constant and loss tangent are affected by frequency of the applied electric field or the frequency of other electromagnetic fields impinging on the material. The polarization requires time to respond to an applied field. Electronic polarization occurs very rapidly and is present even at high frequencies (Richerson et al., 2005).

2.3.2 Capacitance

A capacitor is a component that comprises of dielectric material between two electrically conductive electrodes. When it is placed in an electric circuit, it is able to store electrical charge. Capacitance is the electric property of capacitors. It is defined as a measure of the capacity of storing electric charge for a given voltage. In dielectric material, the higher the degree of polarizability, the higher will be the relative dielectric constant and the more charge that can be stored (Terzic et al., 2012).

The amount of charge (Q) that can be stored is equal to the applied voltage (V) times the capacitance (C) as in Equation 2.1 (Terzic et al., 2012).

$$Q = C\,V \quad \text{………………………...………………} \quad (2.1)$$

The unit of charge Q is the coulomb, which is an ampere-second. The unit of capacitance C is the farad. A capacitor has a capacitance of one farad when one coulomb charges it to an electric potential of one volt. One farad can be considered as a very large level of capacitance (Terzic et al., 2012).

The capacitance depends on the relative dielectric constant *K'* and the geometry of the capacitor. For a parallel-plate capacitor, this relationship is expressed as in Equation 2.2:

$$C = \frac{E_0 K' A}{t} \quad \text{……………………………………(2.2)}$$

Note that the capacitance increases as the area and relative dielectric constant increase and as the thickness of the dielectric decreases (Richerson et al., 2005).

2.3.2 Loss Tangent, tan δ

The loss tangent, tan δ, is a measure of the dielectric losses in the material and a measure of the heat generation capacity of the ceramic when operated under dynamic conditions. It is a direct measurement and is usually formed at the same conditions as the capacitance measurement (Jordan and Ounaies, 2001).

In an ideal dielectric, there is no flow of electric charge, only a displacement of charge via polarization. If a thin plate of such an ideal material was placed between parallel plate electrodes to form a capacitor, the current would lead the voltage by a phase angle of π/2 or 90° if an alternating electric field was applied. Under this circumstance, no power would be absorbed by the dielectric and the capacitor would have zero loss. Real materials always have some loss. The phase angle between the current and voltage is not exactly 90°; the current lags slightly behind what it would be in an ideal dielectric. The angle of lag is defined as δ and the amount of lag becomes *tan δ*. Tan δ is referred to as the loss tangent and is equal to *K''/K'*, where *K'* is the relative dielectric constant and *K''* is defined as the relative loss factor. The dielectric loss and dielectric constant are often higher for polycrystalline materials (Richerson et al., 2005).

Dielectric loss results from several mechanisms include ion migration, ion vibration and deformation, and electronic polarization. Among these, ion migration is the most important mechanism and it is strongly affected by temperature and frequency. The losses due to ion migration increase at low frequencies and as the temperature increases (Abbas and Zake Eldeen, 2014).

2.4 Lead Zirconate Titanate (PZT)

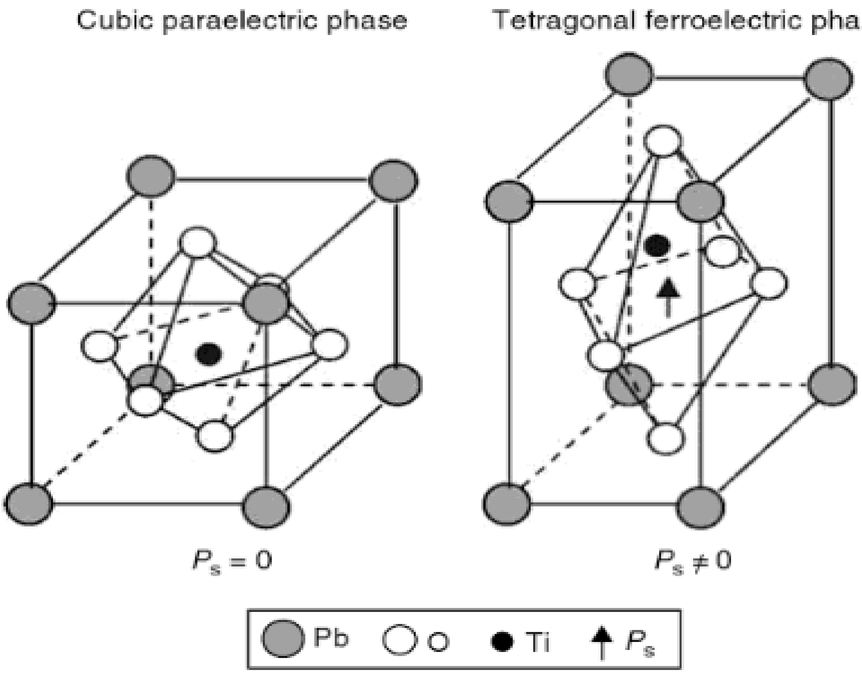
Lead zirconate titanate (PZT) is a polycrystalline ceramic material with chemical formula as $Pb(Zr_xTi_{1-x})O_3$ ($0 < x < 100$). It belongs to perovskite family and can be expressed by the general formula ABO_3, where “A” is a divalent cation (Pb^{2+}) occupies at corners of the cube, “B” is a tetravalent cation (Zr^{4+} or Ti^{4+}) occupies at body centered position and “O” is the oxygen atoms at the face centered positions of the cubic structure. The ionic radii of both lead and oxygen ions are about 1.32 Å and 1.4 Å respectively and together they make a face-centered-cubic array, having a lattice parameter of nearly 4.0 Å (Panda and Sahoo, 2015).

“A” and “B” sites of perovskite can be doped with different ions. The doping of PZT is able to improve the properties of material. This doping at “A” and “B” sites depends only on the sizes of the sites and it is independent of the donor and acceptor properties of foreign ions. The presence of defects can have a strong influence on the electrical and structural properties of PZT (Kamakshi et al., 2015).

Solid solutions between lead zirconate ($PbZrO_3$) and lead titanate ($PbTiO_3$) are known by PZT composition. Pure $PbZrO_3$ and $PbTiO_3$ and their solid solutions are ferroelectric or antiferroelectric and exhibit a permanent electric dipole even in the absence of external electric field. PZTs have never been used in single-crystal form. Those are useful only in ceramic form. The mechanism of piezoelectricity in PZT is somewhat different from single-crystal piezoelectric materials, such as quartz. Macroscopically, they are isotopic due to the random arrangement of the electrical dipoles. A poling process is then applied to produce a permanent electric polarization. After poling, the dipoles are aligned with the poling field and the piece of material becomes anisotropic. A strong piezoelectric effect is generated (Chen, 1993).

2.4.1 Perovskite Structure

PZT is a binary solid solution of $PbZrO_3$ (an antiferroelectric orthorhombic structure and $PbTiO_3$ (a ferroelectric tetragonal perovskite structure). It has a perovkite structure with Pb^{2+} ions occupying the A site while the Zr^{4+} and Ti^{4+} ions occupying the B site of the ABO_3 structure at random as shown in Figure 2.5 (Schwartz, 2008).



(a) (b)

Figure 2.5: Crystal structure of Pb(Zr,Ti)O_3 ceramics, (a) above the Curie point, the cell is cubic and (b) below the Curie point, the cell is tetragonal/rhombohedral (Schwartz, 2008)

Above the Curie temperature (T_c), PZT materials are nonpolar and cubic. However, below the Curie temperature (T_c), it becomes spontaneously electrically polarized and mechanically distorted. Depending on the Zr toTi ratio (Figure 2.6), PZT transforms onto a rhombohedral or a tetragonal phase below T_c, depending on the composition. At the composition where both phases coexist, it is defined as morphotropic phase boundary (MPB). In the $Pb(Zr_xTi_{1-x})O_3$ solid solution, the MPB occurs at around X ~0.535 where the electromechanical properties reach a maximum (Michen, 2011).

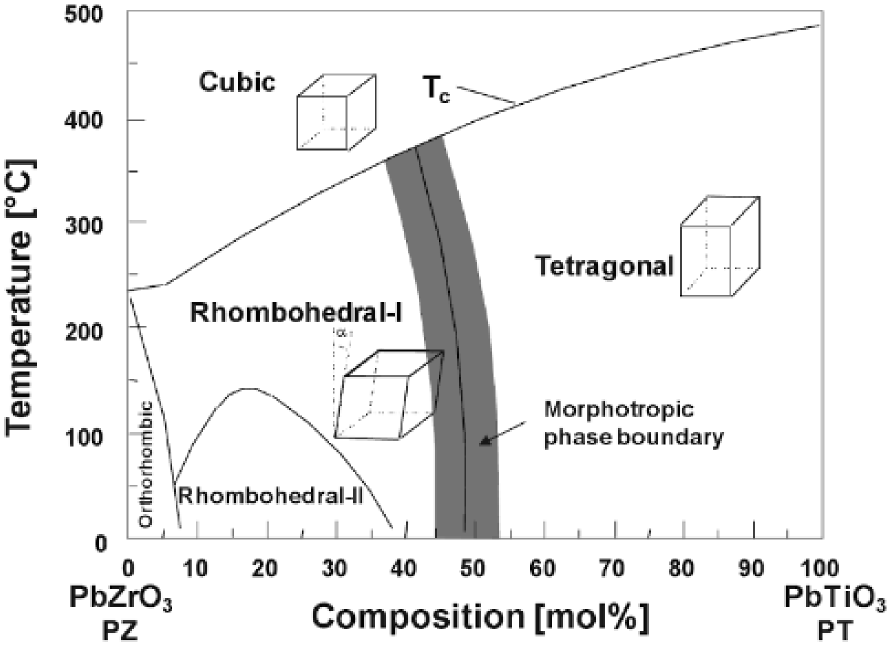


Figure 2.6: Phase diagram of PZT with the grey shaded area shows the coexistence region of the tetragonal and rhombohedral phase (Michen, 2011)

2.4.2 Dopants of PZT

PZT ceramic powders are prepared with dopants and additives incorporated into the perovskite structure in order to tailor the properties for specific applications (Moulson and Herbert, 2003). Substitution can take place using isovalent (e.g., Ba^{2+}, Ca^{2+}, Sr^{2+} on A-sites and Sn^{4+} on B-sites) or aliovalent ions with higher or lower valencies. The common aliovalent dopants in perovskite-type ceramics are listed in Table 2.1. Donor dopants or soft dopants, which have higher charge than that of the ion they replace, are compensated by A-site vacancies in the crystal structure, which enhances domain reorientation (Michen, 2011).

Table 2.1: Common aliovalent substituents (Moulson and Herbert, 2003)

Soft dopants	A-site donors B-site donors	La^{3+}, Bi^{3+}, Nd^{3+} Nb^{5+}, Ta^{5+}, Sb^{5+}
Hard dopants	A-site acceptors B-site acceptors	K^{+}, Rb^{+} Co^{3+}, Fe^{3+}, Sc^{3+}, Ga^{3+}, Cr^{3+}, Mn^{3+}, Mn^{2+}, Mg^{2+}

Acceptors or hard dopants, which have lower charge than that of the replaced ions, are compensated by oxygen vacancies, which reduce domain mobility due to formation of addition dipoles (Michen, 2011). The major effects of different types of dopants are summarized in Table 2.2(Panda and Sahoo, 2015).

Heiber and co-workers (2008) succeeds in synthesizing multiple component systems by tailoring the PZT with dopants or complex perovskite compounds, exhibiting unusual characteristics. An increase of the electromechanical effects and piezoelectric coefficients can be achieved, as well as lower sintering temperatures, lower porosity, higher density, finer and more uniform grains and low loss of PbO. These characteristics are obtained due to heterovalent ion combinations (double substitution of acceptor and donor ions) favors the creation of vacancies at both “A” and “B” sites. This can promote the diffusion process during sintering and achieve an optimum ceramic microstructure and optimum physical characteristics for doped PZT.