EFFECT OF ORGANIC SYSTEM ON PIEZOELECTIC PROPERTIES OF PLZT FABRICATED BY TAPE CASTING

ABSTRACT

BY

JARUWAN THAMPRASIT

Presented in Partial Fulfillment of the Requirements for the

Master of Science Degree in Material Science

at Srinakharinwirot University

July 2017

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The lanthanum doped PZT ($(Pb_{0.9}La_{0.1})(Zr_{0.65}Ti_{0.35})O_3$, PLZT) at the morphotropic phase boundary has a mixture of tetragonal and rhombohedral phases, providing excellent properties for transducer applications. However, the properties of PLZT ceramics depend on fabrication process, chemical composition and sintering conditions. In this study, PLZT pre parathion is the tape casting method with aqoues based slurry. The combination of binder, plasticizer, dispersant and defoamer (organic system) will be varied in decreasing a mounts of organic system for 10-30 wt.%. PLZT tapes are fabricated at several thicknesses. The crystal structure, morphology, composition, electrical properties are also investigated. The reduction of organic system for 10-30 wt.% of PLZT slurry use tape-casting for fabrication by tape casting. The crystal structure of PLZT tape is perovskite polycrystalline with (100), (110), (111), (200), (210) and (211). The microstructure of PLZT tapes has uniform grain shapes and grain sizes with and without decreasing organic systems. More porosities are observed on PLZT tapes with decreasing organic systems. PLZT tapes have an average grain size about 1 μm over the PLZT tape surface. The dielectric constant, capacitance, and the loss of PLZT tapes without decreasing organic system at different thickness of thinner PLZT tapes show higher dielectric constant and capacitance values than thicker PLZT tapes. The dielectric constant of PLZT tapes reveal that PLZT tapes without decreasing organic system show higher dielectric constants than PLZT tapes with decreasing organics system for 10-30 wt. %. In this study, the PLZT tape without decreasing organic system has the highest dielectric constant of 1607 with 6.6% loss at 1 kHz.

ผลของระบบออร์แกนิคที่มีต่อสมบัติไพอิโซอิเล็คทริกของพีแอลซีที ที่ขึ้นรูปแบบเทปคาสติ้ง

บทคัดย่อ

ของ

จารุวรรณ ธรรมประสิทธิ์

เสนอต่อบัณฑิตวิทยาลัย มหาวิทยาลัยศรีนครินทรวิโรฒ เพื่อเป็นส่วนหนึ่งของการศึกษา
ตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต สาขาวิชาฟิสิกส์
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จารุวรรณ ธรรมประสิทธิ์. (2560). *ผลของระบบออร์แกนิคที่มีต่อสมบัติไพอิโซอิเล็คทริกของพีแอลซีทีที่ขึ้นรูปแบบเทปคาสติ้ง*. ปริญญานิพนธ์ วท.ม. (วัสดุสาสตร์). กรุงเทพฯ: บัณฑิตวิทยาลัย มหาวิทยาลัยศรีนครินทรวิโรฒ. คณะกรรมการควบคุม: อาจารย์ ดร.ปัทมาศ บิณฑจิตต์.

การเจือแลนทานัมลงใน PZT เป็น ($Pb_{0.9}La_{0.1}$) ($Zr_{0.65}Ti_{0.35}$) O_3, PLZT) ที่บริเวณ morphotropic phase boundary (MPB) ซึ่งเป็นบริเวณที่มีการผสมกันของโครงสร้างแบบ tetragonal และ rhombohedral และมีคุณสมบัติไพอิโซอิเล็กทริกที่ดีเยี่ยมซึ่งถูกนำมาประยุกต์ใช้งานในทรานสดิวเซอร์ (transducer) แต่อย่างไรก็ตามคุณสมบัติของ PLZT นั้นขึ้นอยู่กับกระบวนการผลิต องค์ประกอบทางเคมี และเงื่อนไขในการเผาผนึก ในงานวิจัยนี้ได้ใช้กระบวนการเทปคาสติ้ง (tape casting) โดยมีน้ำเป็นองค์ประกอบ ในการขึ้นรูปแผ่น PLZT โดยส่วนผสมของสเลอรีประกอบด้วยตัวประสาน สารเพิ่มความเหนียว สารช่วยกระจายตัว และ สารลดฟอง (ระบบออร์แกนิค) โดยมีการปรับลดระบบออร์แกนิคลง 10-30 wt.% และมีการเตรียมแผ่น PLZT ที่หลายความหนา จากนั้นศึกษาโครงสร้างผลึก โครงสร้างจุลภาค ลักษณะพื้นผิว และสมบัติทางไฟฟ้าของแผ่น PLZT พบว่าการปรับลดระบบออร์แกนิคลง 10-30 wt.% สามารถขึ้นรูปแผ่น PLZT ด้วยกระบวนการ tape casting ได้ โครงสร้างผลึกของแผ่น PLZT เป็นแบบ Perovskite Polycrystalline โดยมีระนาบ (100) (110) (111) (200) (210) และ (211) ตามลำดับ พื้นผิวของแผ่น PLZT ที่ไม่มีการที่ปรับลดและมีการปรับลดระบบออร์แกนิคลงพบว่ารูปร่าง และขนาดของเกรนมีขนาดเท่ากัน และแผ่น PLZT ที่มีการปรับลดระบบออร์แกนิคลงจะเกิดฟองอากาศมากบนพื้นผิวของแผ่น PLZT เมื่อเปรียบเทียบกับแผ่น PLZT ที่ไม่มีการที่ปรับลดระบบออร์แกนิค ขนาดเกรนโดยเฉลี่ยอยู่ที่ประมาณ 1 μm กระจายตัวอยู่บนแผ่น PLZT แผ่น PLZT ที่ไม่มีการลดระบบออร์แกนิคที่ความหนาน้อยกว่า มีค่าสภาพยอมสัมพัทธ์ ค่าความจุไฟฟ้า และค่าความสูญเสียไดอิเล็กทริกมากกว่าแผ่น PLZT ที่หนากว่า ส่วนแผ่น PLZT ที่ไม่มีการลดระบบออร์แกนิคลงมีค่าสภาพยอมสัมพัทธ์ และค่าความจุไฟฟ้าสูงกว่าแผ่น PLZT ที่ไม่มีการลดของระบบออร์แกนิคลง10-30 wt.% ในงานวิจัยนี้แผ่น PLZT ที่ไม่มีการลดของระบบออร์แกนิคมีค่าสภาพยอมสัมพัทธ์สูงที่สุดเท่ากับ 1607 และมีค่าความสูญเสียไดอิเล็กทริกเท่ากับ 6.6% ที่ 1 kHz

The thesis titled

“Effect of organic system on piezoelectric properties of PLZT fabricated by tape casting”

by

Jaruwan Thamprasit

has been approved by the Graduate School as partial fulfillment of the requirements for the Master of Science Degree in Material Science of Srinakharinwirot University.

…… Dean of Graduate School

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Month …….Date ……..,Year ……

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Jaruwan Thamprasit

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CHAPTER 1

INTRODUCTION

Background

The piezoelectric materials based on Lead Zirconate Titanate (PZT) are the most widely used in smart ceramics. They are employed for sensor, actuator, and transducer applications. For example, PZT is used as actuator to control read-write head in Hard Disk Drives (HDDs) devices. The ratio of Zr/Ti (52/48) of PZT at the morphotropic phase boundary (MPB) performed the high piezoelectric responses. In addition, PZT can be modified and used for other applications such as optic applications by doping with specific elements.

Doped piezoelectric ceramics are categorized by two types, which are “hard” and “soft” piezoelectric ceramics. Hard piezoelectric ceramics have smaller piezoelectric constants, lower permittivity, low dielectric constant with low dielectric losses, low electromechanical coupling factors, high mechanical quality factors and difficult in polarization with high coercive field. Hard PZT can be exposed to high electrical and mechanical stresses. In contrast, soft piezoelectric ceramics have larger piezoelectric constants, higher permittivity, larger dielectric constants and losses, larger electromechanical coupling factors, low coercive field resulting in easier polarization. The high power applications such as ultrasonic devices employed soft piezoelectric ceramics with high domain mobility resulted from easy polarization such as actuators and low power transducer applications.

In this research, the La^{3+} donor dopant into PZT was studied. Perovskite Lead Lanthanum Zirconate Titanate (PLZT) ceramics have the chemical formula as $Pb_{(1-X)}La_X(Zr_yTi_{(1-y)}O_3)$. The La^{3+} was doped into PZT and the La^{3+} dopant could improve the elctro-optic properties of PZT. Lanthanum is a donor dopant in PZT with La^{3+} substitution on Pb site giving the structure defect. PLZT materials are high density, transparency products with useful electro-optic properties, which is used as the basis of the optical memories.

The PLZT composition at the morphotropic phase boundary has a mixture of tetragonal and rhombohedral phases providing the excellent properties for the transducer applications. Moreover, PLZT was good transparency from the visible light to the near-infrared and has high refractive index. Therefore, PLZT ceramics have been employed for optical devices. The properties of PLZT ceramics depend on fabrication process, chemical composition and sintering conditions.

In this study, $(Pb_{0.9}La_{0.1})$ $(Zr_{0.65}Ti_{0.35})$ O_3 was chosen because this composition provides the mixture of the rhombohedral and tetragonal ferroelectric phases. PLZT with this composition (0.9/65/35) is a relaxor ferroelectric which has large dipole moment with large mechanical strain. Also, PLZT is temperature dependence of small hysteretic at transition region. The PLZT was prepared by tape casting method. Tape casting method has been used to prepare ceramic sheet for several electronic applications.

There are two types of slurry preparation: solvent based slurry and aqueous based slurry. In the past, solvent based was mainly used for tape casting method due to their low latent heat of evaporation and low surface tension. Organic additives control the stability of slurry as well as strength and flexibility of green tapes. Recently, the aqueous slurry was used because of non toxicity, environmental safety, and low cost. However, the uniform green tapes prepared by aqueous based slurry were more difficult to achieve than solvent based because of high surface tension[14].

In this research, the combination of binder, plasticizer, and defoamer (organic system) will be varied and studied. The PLZT samples will be fabricated with several thicknesses. The crystal structure, morphology, composition, electrical properties will be investigated in this research.

Objective of the study

1. To study PLZT ceramics, PLZT applications, and tape casting method.
2. To fabricate PLZT by tape casting method with different thickness.
3. To study the effect of organic system on the tape casting fabrication of PLZT.

4. To study the effect of organic system on microstructure and electrical property of PLZT fabricated by tape casting method.
5. To characterize phase and microstructure of PLZT fabricated by tape casting.

Significance of the Study

To understand electrical properties of PLZT by tape casting affected by different thickness and different organic system contents.

Scope of the Study

The organic system contents (binder, plasticizer, and defoamer) and the PLZT with different thickness were studied in this research. The crystal structure, microstructure and electrical properties of PLZT were investigated.

Definition of terms

1. HDDs (Hard Disk Drives)
2. PZT (Lead Zirconate Titanate)
3. PLZT (Lead Lanthanum Zirconate Titanate)
4. BT (Barium titanate)
5. TC (Curie Temperature)
6. MPB (Morphotropic Phase Boundary)
7. E_C (Coercive field)
8. P_r (Remanent polarization)
9. Ps (Spontaneous polarization)
10. k_P (Electromechanical Coupling Coefficient)
11. d_{31}, d_{33} (Piezoelectric Coefficient)
12. ε_r (Relative permittivity of the material or Dielectric constant)
13. ε_0 (Permittivity of a vacuum or the permittivity of free space)
14. XRD (X-Ray Diffraction)
15. FE-SEM (Field Emission Scanning Electron Microscope)
16. EDS (Energy Dispersive X-Ray Spectrometer)
17. LCR (Inductance (L), Capacitance (C), and Resistance (R))

CHAPTER 2

REVIEW OF THE LITERATURE

In this chapter, the concept of dielectric, piezoelectric, ferroelectric materials followed by the PZT materials, PLZT and ceramic processing are discussed as follows:

2.1 Dielectrics, Piezoelectrics and Ferroelectrics Materials

2.1.1 Dieletric Materials

2.1.2 Piezoeletric Materials

2.1.3 Ferroelectric Materials

2.1.4 Pyroelectric Materials

2.1.5 Point Groups Symmetry

2.1.6 Perovskite Structure

2.2 PZT and PLZT

2.2.1 Morphotropic Phase boundary (MPB)

2.2.2 Doped PZT

2.2.3 Phase diagram of PZT-PLZT solid-solution system

2.2.4 PLZT

2.3 Ceramic Processing

2.3.1 Tape Casting, fabrication method

2.4 Literature review of PLZT

2.1 Dielectrics, Piezoelectric, and Ferroelectrics Materials

2.1.1 Dielectric materials

Dielectric materials are insulating materials and do not permit charges to pass through. Electrostatic effects occur in the dielectric materials, which lead to the creation or modification of dipole moments. Dielectric materials present permanent electric dipole moments and enhance the capacitance. FIGURE 1 shows the typical capacitor and capacitor with dielectric material [1].

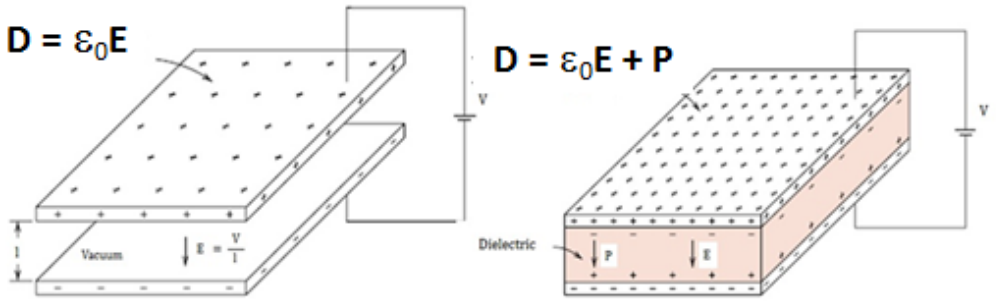


Figure 1 Schematic illustrations for (a) capacitor plates and (b) capacitor plates with dielectric material [1]

The capacitance of dielectric materials can be calculated by EQUATION 2-1 to 2-3.

$$C = \varepsilon \frac{A}{l}$$ EQUATION 2-1 [1]

$$C = \varepsilon_0 \varepsilon_r \frac{A}{l}$$ EQUATION 2-2 [1]

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$$ EQUATION 2-3 [1]

The capacitances of the capacitors in parallel and series are calculated by EQUATION 2-4 and 2-5, respectively.

$$C = C_1 + C_2 + C_3$$ EQUATION 2-4

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3}$$ EQUATION 2-5

Where

ε_0 = permittivity of a vacuum or the permittivity of free space = 8.854 x 10^{-12} F/m

ε_r = relative permittivity of the material or dielectric constant

C = capacitance (F)

A = plate area (m^2)

l = distance between plates (m)

When the electric field is applied to dielectric materials, dipole moments are polarized. There are four polarization mechanisms: electronic polarization, ionic polarization, dipolar polarization and space charge polarization, as shown in FIGURE 2 [2].

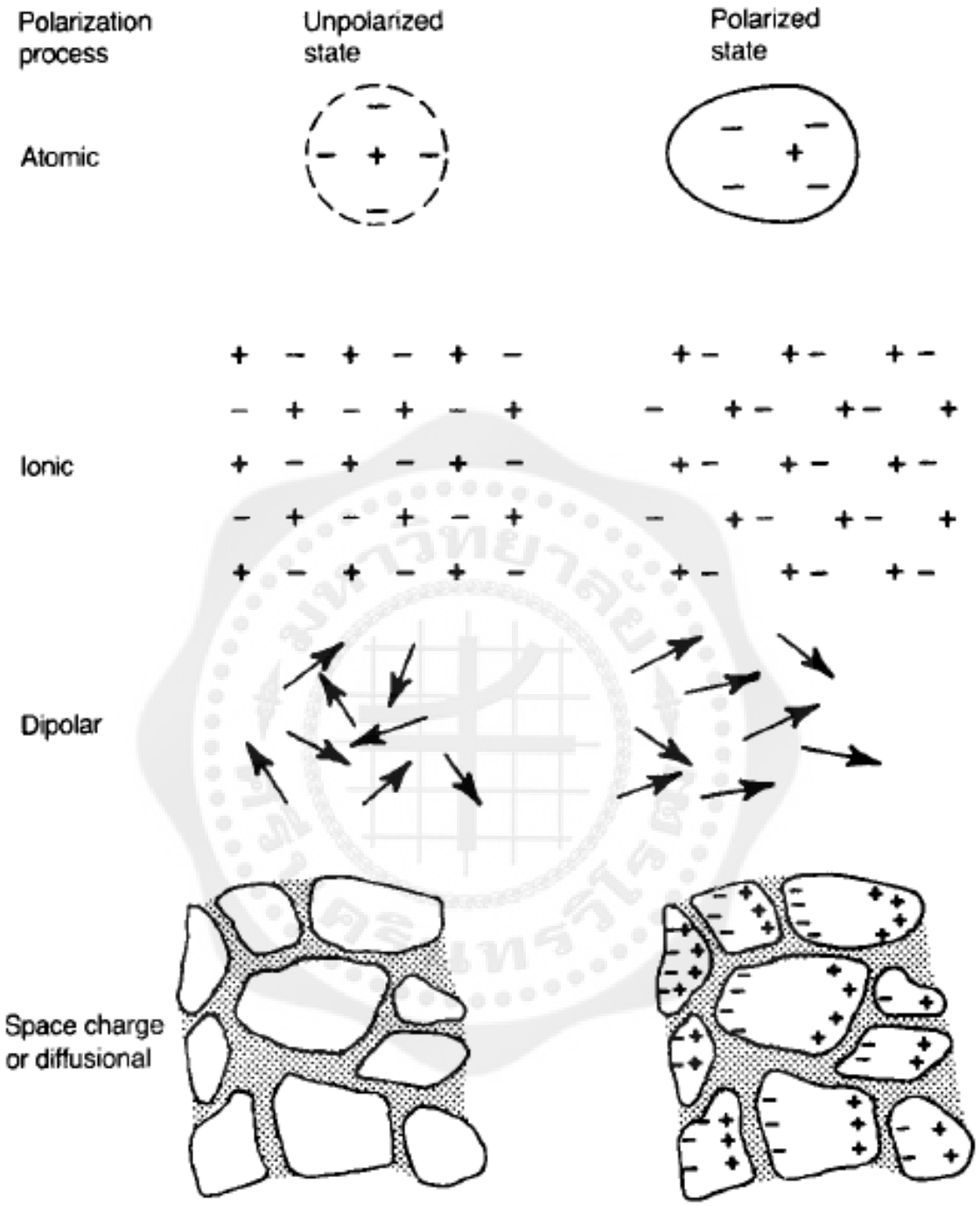


Figure 2 Schematic representation of four mechanisms of polarization [2]

FIGURE 3 shows the frequency dependence of the dielectric constant on real part and imaginary parts. The electrostrictive effects result from the dipole moment arising from ion displacements.

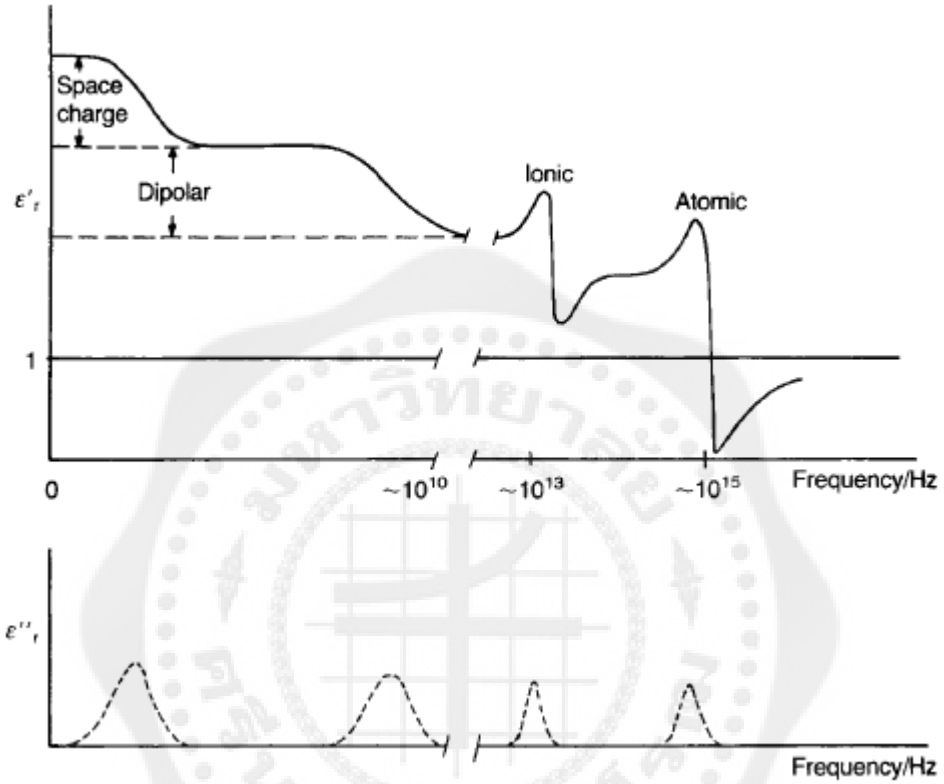


Figure 3 The relative permittivity as a function of frequency [2]

2.1.2 Piezoelectric Materials

Piezoelectric materials can convert electrical energy to mechanical energy or mechanical energy to electrical energy. There are two piezoelectric effects. When mechanical stress is applied to piezoelectric materials, dipoles are polarized known as direct piezoelectric effect (FIGURE 4 (a)). In contrast, the piezoelectric crystal becomes strained, when electric field is applied that is converse piezoelectric effect (FIGURE 4 (b)).

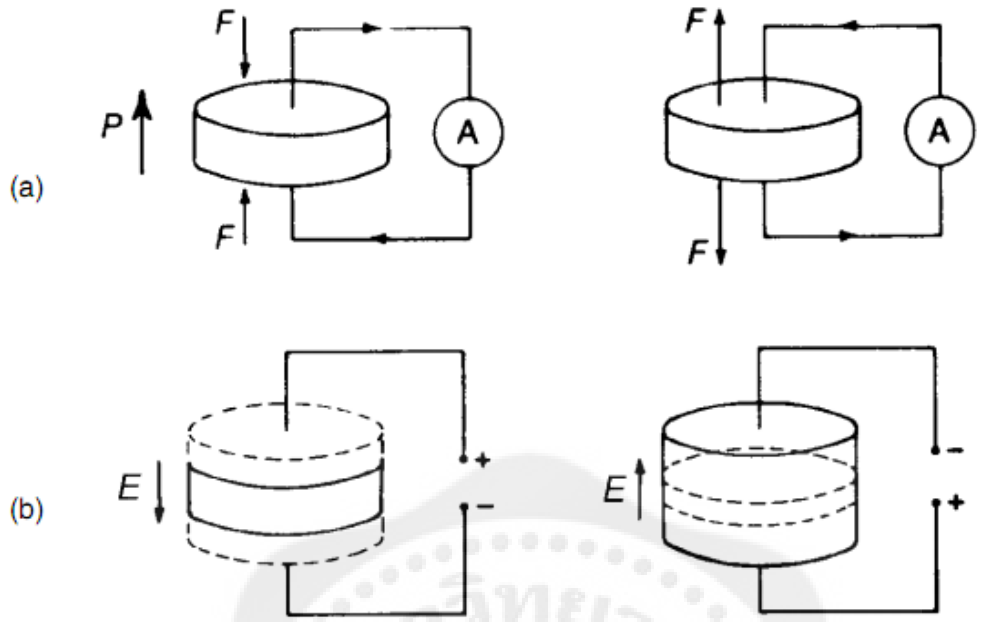


Figure 4 Schematic of piezoelectric effects, (a) direct piezoelectric effect, and (b) converse piezoelectric effect [2]

The parameters for the piezoelectric effect are strain, stress, electric field and electric displacement.

The materials produce the dielectric displacement that is linearly relative to an applied mechanical stress shown in EQUATION 2-6 and known as direct piezoelectric effect.

$$\mathbf{D_i} = \sum_k \mathbf{d_{ik}}\, \boldsymbol{\sigma}_k \qquad \text{EQUATION 2-6 [3]}$$

In contrast, the converse piezoelectric effect that the strain is relative to an applied electric field shown as EQUATION 2-7

$$\mathbf{X_i} = \sum_k \mathrm{d_{ki}}\, \mathbf{E_k} \qquad \text{EQUATION 2-7 [3]}$$

Where

D_i = dielectric displacement (i = 1 to 3)

X_i = strain (i = 1 to 6)

σ_k = stress (i = 1 to 6)

E_k = electric field (i = 1 to 3)

d_{ik} or d_{ki} = piezoelectric coefficient

The applications of the direct piezoelectric effect and the converse piezoelectric effect are sensor and actuator applications, respectively [3].

2.1.3 Ferroelectric Materials

Both natural and synthetic materials can behave piezoelectricity such as quartz, barium titanate, lead titanate, lithium niobate, and lead zirconate titanate. Lead zirconate titanate (PZT) is the most superior piezoelectric, ferroelectric, and pyroelectric ceramics. Ferroelectrics are both pyroelectric and piezoelectric. They have spontaneous polarization that can be reoriented with an electric field. The polarization can exist even when the external electric field is removed. FIGURE 5 shows the P-E hysteresis loop (polarization as a function of the electric field) of ferroelectric materials in cases of single crystal (FIGURE 5 (A)) and polycrystalline (FIGURE 5 (b)).

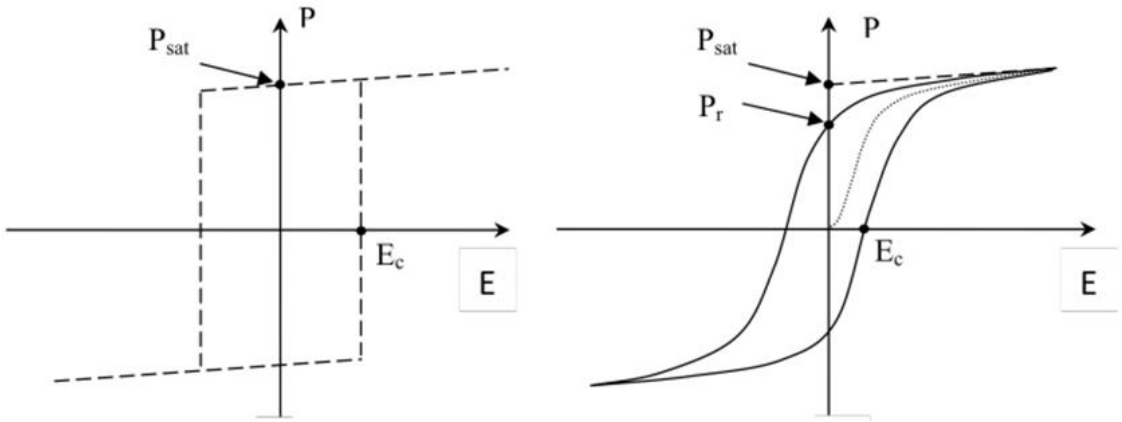


Figure 5 A polarization – electric field hysteresis loop, (a) Ideal single crystal, and (b) Polycrystalline [3]

In the P-E hysteresis loop of ferroelectric materials, there are different domain contributions related to polarization at various applied electric fields (FIGURE 6). Domain is the area or volume that dipoles have the same polarization. Domain wall is the boundary between different polarizations. With an un-poled sample (point O), there are no polarizations (P = 0). After that, an electric field was applied to induce polarization until the domains are aligned to an applied electric field with a perfect poled state (point A). The remanent polarization (P_r) is some of reverse domains and they cannot return to the original configuration when an electric field becomes zero (point B). When increased electric field with the reverse polarity, it appears the reversed polarization directions and becomes perfect poled state in another direction (point E). When electric field becomes zero (point F), there is the remanent polarization (point F). As an increased applied electric field, the polarization becomes perfect poled state again (point A) [3].

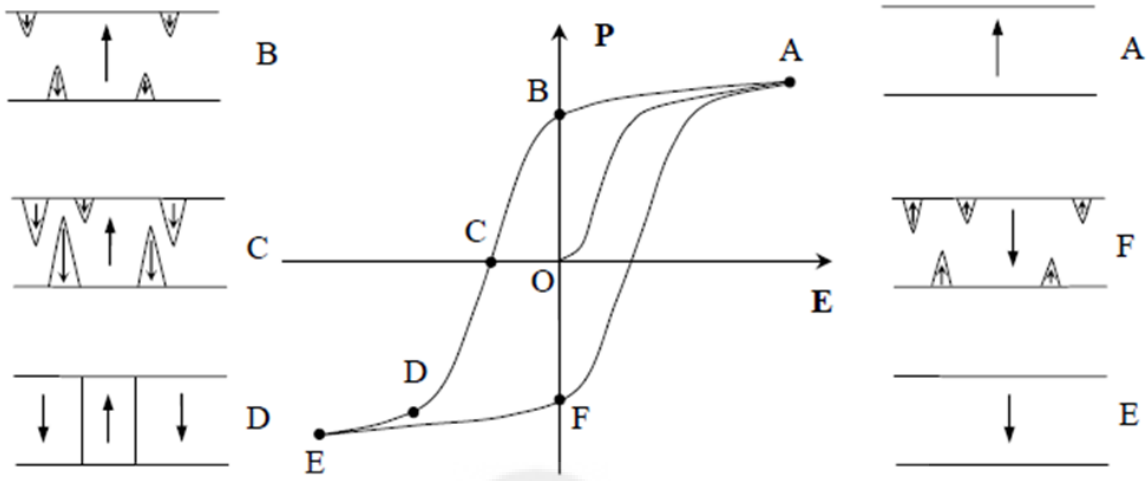


Figure 6 P-E Hysteresis loop and domain configuration of ferroelectric crystal [3]

2.1.4 Pyroelectric Materials

Pyroelectric are materials response between temperature and polarization that the pyroelectricity is the temperature dependence of the spontaneous polarization P_s of polar piezoelectric materials.

Pyroelectricity is the ability of materials to produce a permanent voltage when varying the temperature. The change in temperature changes the positions of the atoms slightly within the crystal structure resulting in changing the polarization. This polarization changes develop a voltage across the crystal. If the temperature is constant at its new value, the pyroelectric voltage disappears due to leakage current.

The pyroelectric materials are polar and piezoelectric. The strain is induced from thermal expansion resulting in the development of surface charges. However, this is less effect and does not more than 10% of the primary pyroelectric effect.

FIGURE 7 shows the pyroeletric coefficient as a function of temperature. At very low temperature, the pyroelectric coefficient becomes zero because thermal motions drop [4].

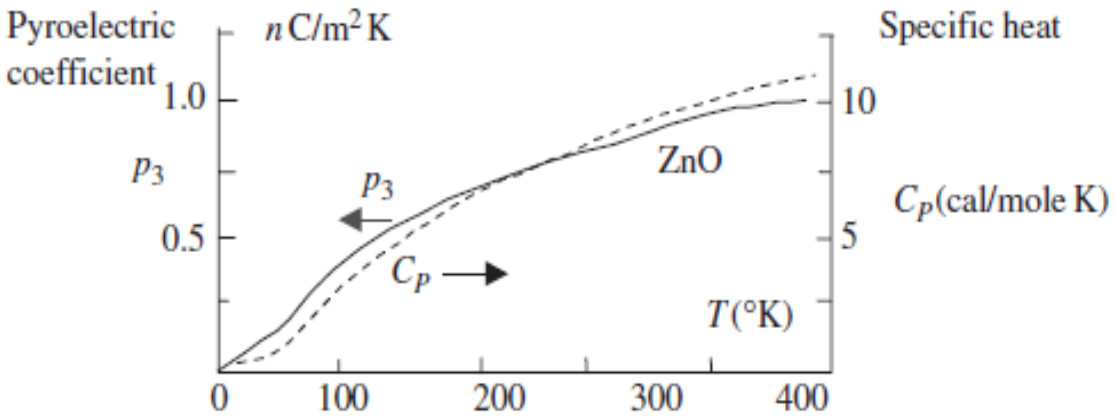


Figure 7 Temperature dependence of pyroelectric coefficient [4]

2.1.5 Point Groups Symmetry

Symmetry is important for materials to behave either piezoelectric or non-piezoelectric. There are categorized to 32 crystallographic point groups, as shown in FIGURE 8. There are 11 point groups are centrosymmetric and 21 point groups are non-centrosymmetric. In 21 non-centrosymmetric point groups, only one is non-piezoelectric while there are 20 piezoelectric. For 20 piezoelectric point groups, there are 10 groups, which behave pyroelectric. Ferroelectrics are sub-group of the pyroeletric group. Ferroelectric have spontaneous polarization that can be reoriented with an applied electric field. Therefore ferroelectric materials must be both pyroelectric and piezoelectric materials [4].

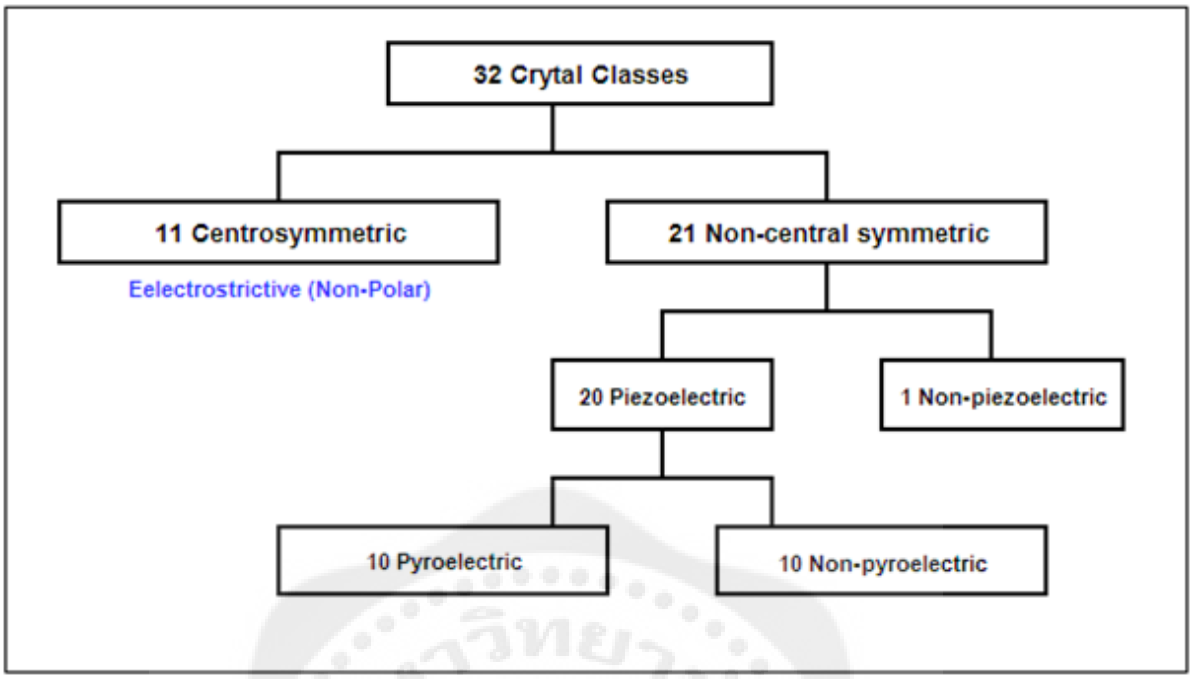


Figure 8 The 32 point groups [4]

2.1.6 Perovskite Structure

Perovskite is structure of piezoelectric materials such as lead zirconate titanate ($Pb(Zr_xTi_{1-x})O_3$: PZT) and barium titanate ($BaTiO_3$). FIGTURE 9 shows the perovskite crystal structure of lead zirconate titanate. The chemical formula of perovskite structure is ABO_3 that is a cubic closed pack structure. There are two cations at A and B sites that the cation A is bigger than the cation B. O is an anion that bonds to both cations. In case of PZT, Pb^{2+} ions locate at the 8 corners of unit cell, Zr^{4+} ions and Ti^{4+} ion locate at the center of unit cell, and O^{2-} locate at the center of 6 faces of the unit cell [3].

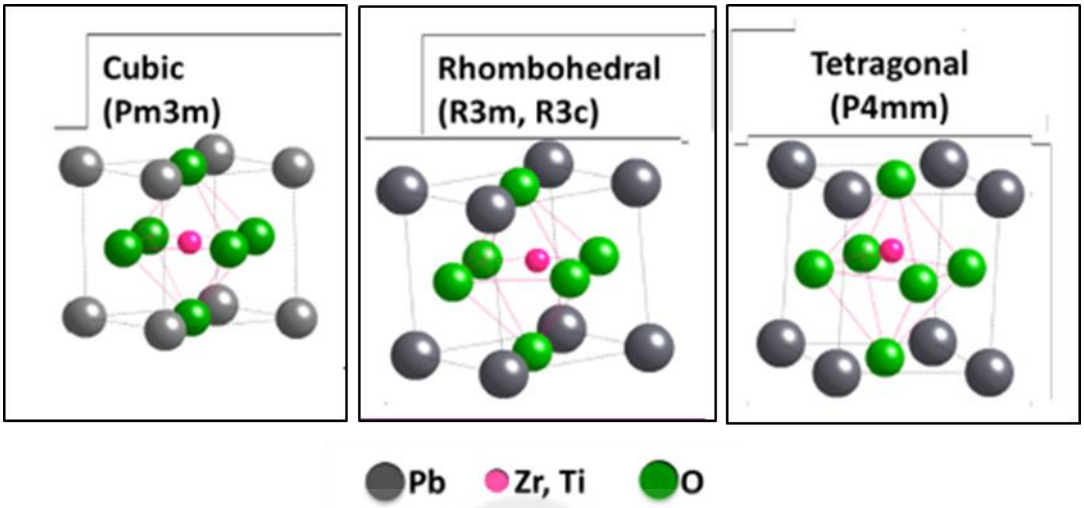


Figure 9 Perovskite crystal structure of PZT (a) cubic structure, (b) tetragonal structure, and (c) rhombohedral structure [3]

2.2 PZT and PLZT

2.2.1 Morphotropic Phase Boundary (MPB)

The phase diagram of $Pb(Zr_{1-x}\ Ti_x)O_3$ (PZT) is shown in FIGURE 10. The crystal structure of PZT depends on the composition of solid solution $PbZrO_3$ – $PbTiO_3$, significantly. At the morphotropic phase boundary (MPB), there are structural changes. In FIGURE 11, the piezoelectric at the MPB composition shows highest relative permittivity, highest ε_r and highest electromechanical coupling factor, k_P.

Morphotropic Phase Boundary (MPB) of the PZT material is the boundary between tetragonal and rhombohedral crystal structure. The Curie temperature (T_C) of PZT is 390°C. The PZT crystal structure is cubic at temperatures above T_C while at below T_C, the crystal structure distorts to either a tetragonal or rhombohedral structure depend on the ratio of $PbZrO_3$ and $PbTiO_3$ composition. The piezoelectric and ferroelectric properties of PZT strongly depend on the composition. The maximum of the relative permittivity (ε_r) and electromechanical coupling coefficient (k_P) are at MPB composition [5].

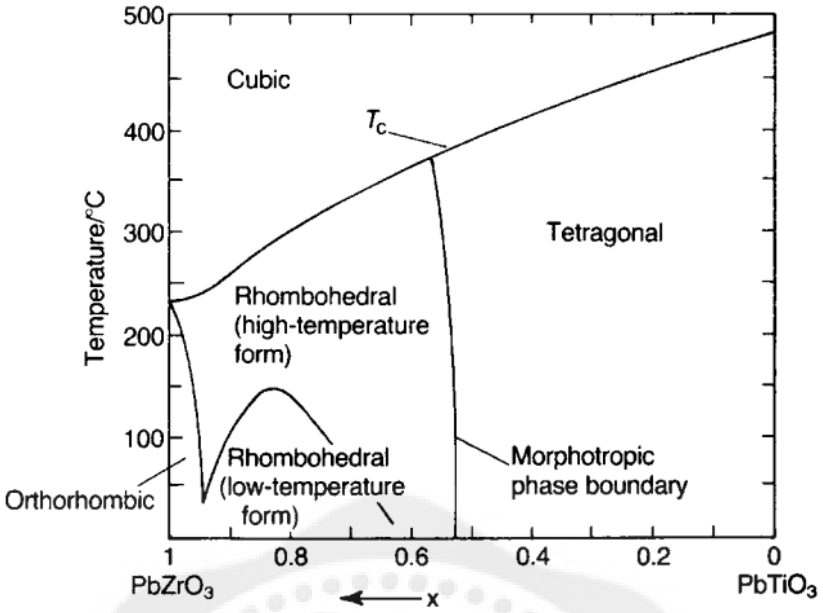


Figure 10 PZT phase diagram ($PbZrO_3$-$PbTiO_3$ solid solution) [5]

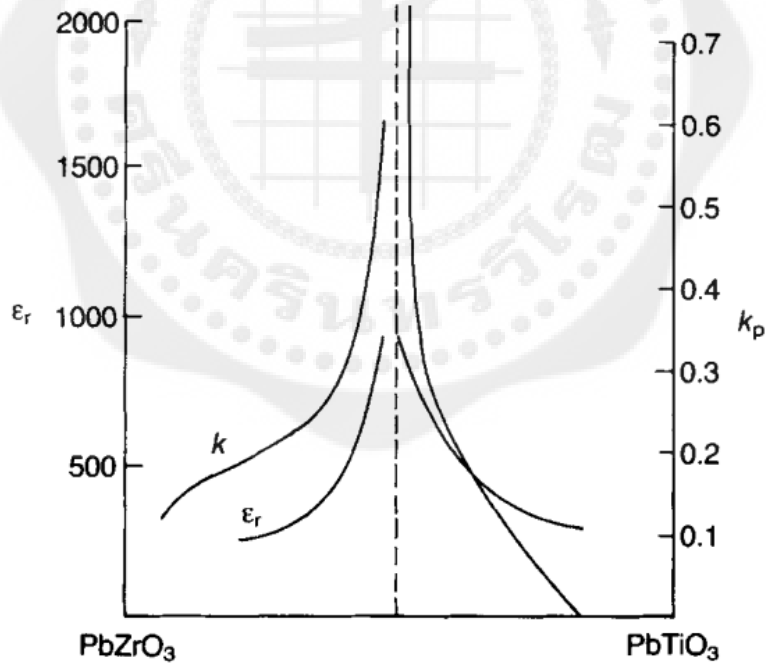


Figure 11 The relative permittivity dependence on composition of $PbZrO_3$-$PbTiO_3$ [5]

(Relative permittivity, ε_r and electromechanical coupling factor, k_p) in PZT

2.2.2 Doped PZT

The PZT ceramics can be modified by the addition of a specific element (dopants) for improving or optimizing the properties for specific applications. Even though the maximum piezoelectric effect is observed at the MPB, the doped PZT materials develop small dielectric loss, a high sharpness of resonance frequency under high electric field and high electro-mechanical coupling coefficient (k_p) and high relative permittivity (ε_r).

Basically, many types of dopants have been added to PZT. The dopants such as La^{3+} affect the piezoelectric properties of PZT. With La^{3+} replace Pb^{2+} giving the structure defects that La^{3+} charges are compensated by A site vacancy. The defects increase the electrical resistivity and modify ferroelectric properties [6].

The dopants ($\geq$5 %) are substitution as solid solution in PZT system. The enhancement in dielectric, piezoelectric, pyroelectric, ferroelectric and electro-optic properties can be obtained [5]. However, the lanthanum dopants in PZT system (PLZT) are attractive in electro-optic properties for sensor and actuator applications. Table 2-1 shows the effect of dopant added to PZT system [7].

Table 1 The effect of dopants to PZT [7]

Specific Dopants				Main Effect
Type	**Replaced site**	**Atom**	**Atomic Radius**	
Soft-dopants (off-valent donor)	Pb^{2+}	La^{3+}	0.122	High permittivity Higher k_p Resistivity 10^3 higher
		Nd^{3+}	0.155	
		Sb^{3+}	0.09	
		Th^{4+}	0.11	
	Ti^{4+} or Zr^{4+}	Nb^{5+}	0.069	
		Ta^{5+}	0.068	
		Sb^{5+}	0.063	
		W^{5+}	0.065	
Isovalent	Pb^{2+}	Ba^{2+}	0.134	Low curie point (T_c) Higher permittivity
		Sr^{2+}	0.012	
	Ti^{4+} or Zr^{4+}	Sn^{4+}	0.071	
Hard-dopants (off-valent acceptor)	Pb^{2+}	K^{+}	0.133	Low permittivity lower k_p lower dielectric loss
		Na^{+}	0.094	
	Ti^{4+} or Zr^{4+}	F^{3+}	0.067	
		Al^{3+}	0.057	
		In^{3+}	0.092	
		Cr^{3+}	0.064	

PZT doped with La^{3+} is known as soft PZT. La^{3+} replaces Pb^{2+} at A site. The donor is compensated by A site vacancies. This dopant provides domain reorientation. The La^{3+} dope should produce the lower distortion of the unit cell. The soft donor provides high permittivity, higher electromechanical coupling factor and higher resistivity [7].

Isovalent additive such as Ba^{2+} replaces Pb^{2+} at A site. The donor is substituted with some vacancies and approximately the same size. These additive inhibits domain reorientation. The isovalent provides low Curie point (T_c) and higher permittivity [7].

Hard donor such as Fe^{3+} replaces Zr^{4+} or Ti^{4+} at B site. The donor is compensated by oxygen vacancies that have limited solubility in the lattice. The hard donor provides low permittivity, lower electromechanical coupling factor and lower dielectric loss [7].

2.2.3. Phase diagram of the PZT-PLZT solid-solution system

The modification of PZT system by doping with Lanthanum (La^{3+}) modifies various properties of the materials. The PLZT phase diagram is shown in FIGURE 12 [8].

where Y axis is the percentage of the occupied La sites and

Z axis is the percentage of the $PbZrO_3$ (Zr atom)

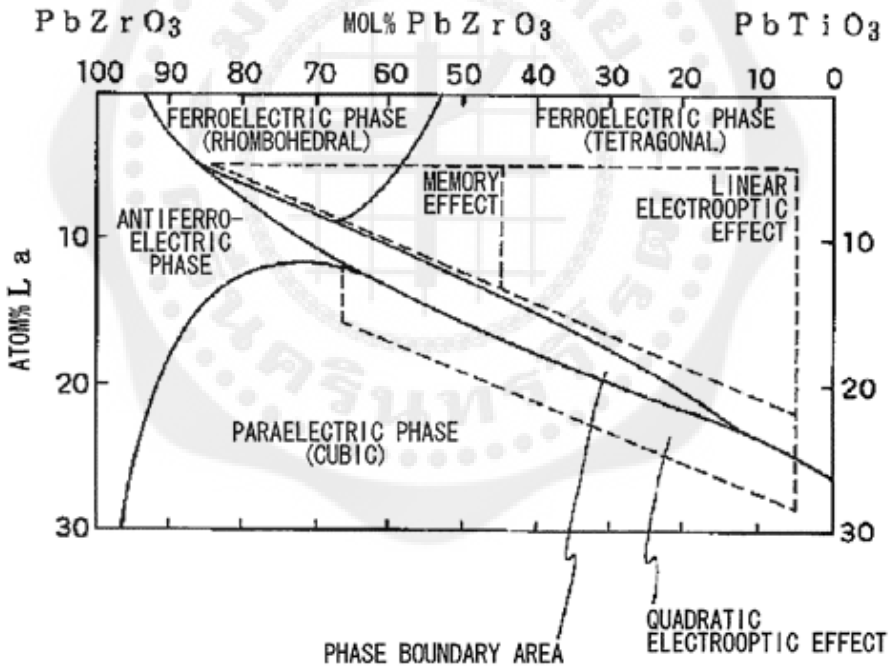


Figure 12 Phase diagram of the $PbTiO_3$-$PbZrO_3$ solid solution dope La^{3+} [8]

The PLZT phase diagram can be divided into three effect regions: quadratic effect, memory effect, and linear effect. Firstly, the quadratic effect region is the phase boundary that separates ferroelectric and paraelectric phases. Secondly, the memory effect region provides the stable compositions and can switch to optical states in the ferroelectric (FE)

rhombohedra phase region. Thirdly, the linear region performs electro-optic effects with the tetragonal phase [8].

2.2.4. PLZT

Perovskite Lead Lanthanum Zirconate Titanate (PLZT) ceramics have the chemical formula $Pb_{(1-X)}\ La_X\ (Zr_yTi_{(1-y)}O_3)$. The La^{3+} was doped into PZT and the La^{3+} dopant could improve the elctro-optic properties by La^{3+} substitution on Pb^{2+} giving the structure distortion. The La^{3+} dopant for PLZT materials is a high density, transparency product with useful electro-optical properties. Moreover, PLZT exhibits good transparency from the visible light to the near-infrared and has high refractive index. Therefore, PLZT ceramics have been employed for optical devices [6].

The temperature and frequency dependence of the dielectric properties of ferroelectric materials provide an information for transducer characteristics such as electrostrictive and electro-optic effects that both are results of dipole moment from ion displacements. As temperature is increased, the relative permittivity increases due to the mobility of domains and the relative permittivity decreases with increased frequency [6].

However, to obtain the superior properties of PLZT ceramics, the processing of PLZT fabrication is very important. PLZT material powders should be made from a chemical co-precipitation technique because the PLZT ceramics require high purity, homogenous, and high-reactivity than other non-optic materials. The optical properties are more sensitive than electrical properties [6].

2.3. Ceramic processing

Composition, purity, material shape, material size, particle size distribution of raw materials must be chosen carefully to achieve good ceramic products and ceramic applications. There have been many processing parameters such as mixing method, casting method, and heat treatment [9].

There have been four steps of ceramic powder processing: powder preparation, shape forming, high temperature sintering and component finishing as shown in FIGURE 13 [7].

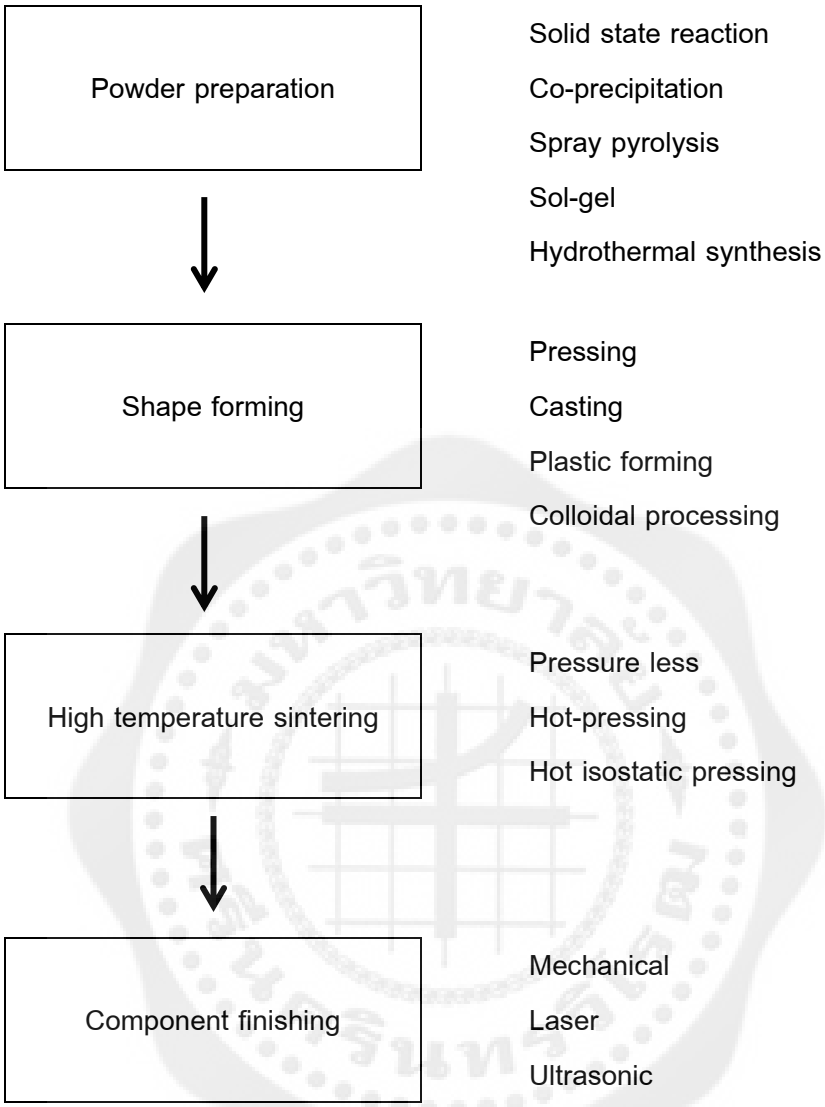


Figure 13 Four steps of ceramic processing [7]

2.3.1 Tape casting, fabrication method

There are many ceramics processing such as slip casting, tape casting, extrusion, pressing, etc. depend on the desire shape and desire applications of ceramics. Tape casting is a method for preparing ceramic tapes. Multilayer ceramic materials can be fabricated via tape casting method. The PZT ceramics prepared by tape casting method have been widely used in the electronics industry such as hard disk drive, electrostrictive devices, capacitors and, ferromagnetic memory ceramics. Tape casting process offers the

wide thickness range and more layers of ceramics. The parameters affecting the tape casting are lamination method, thickness of green tape and shrinkage after sintering process.

The tape casting ingredients consist of as follows: [10]

(i) Ceramic powder or Active powder: the particle size, particle distribution and surface area should be considered. They can affect the microstructure and properties of tape.

(ii) Solvent: the ceramic powder from solid phase will be in a liquid phase by solvent. The solvent must not react easily with ceramic powder and does evaporate easily after sintering process. There are two types of solvent: aqueous solution and non-aqueous solution.

(iii) Dissolved binder: binder is a solution that used for binding the ceramic powder together with a chemically cohesive or mechanically adhesive.

(iv) Plasticizer: it is a substance to optimize flexibility. The plasticizer is added to the mixture of powder, solvent, and binder. The main objective of plasticizer is to increase the flexibility of green tape.

(v) Dispersant: it is the substance for the forming stabilization. Dispersant is either a non-surface active compound or an active substance. It can be added to a the mixture, to increase the separation of particles and to prevent particle clumping.

(vi) Defoamer or an anti-foaming agent: it is an additive for reducing bubble or foam in the mixture or breaking foam that are formed. In addition, the defoamer can reduce the porosity of the green tape.

The whole processes of PLZT ceramic in this research are that the green tapes were manufactured by tape casting. Slurry was prepared by mixing raw materials, binder, plasticizer, and solvent. After that, slurry were ball-milled at about 5 h. After that, the slurry was casted by the hand cast to be the green tape (FIGURE 14), dried under room temperature for 24 h and sintered at 1100°C for 30 min.

Figure 14 Model of hand tape casting of PLZT

2.4. Literature review of PLZT

There are many factors related to the piezoelectric properties of PLZT fabricated by tape casting. For examples: composition, temperature, frequency and sintering temperature etc.

Sabat [6] studied the temperature dependence of the relative permittivity of relaxor ferroelectric PLZT with composition (9.5/65/35). As temperature is increased, the relative permittivity also increased. And the relative permittivity is decreased with increasing frequency. They found that decreasing the temperature increased the hysteresis gap rather than decrease the hysteresis gap. The maximum of relative permittivity of PLZT is 9000.

Hu et al. [11] studied relaxor behavior of ferroelectric PLZT thin films with different Zr/Ti ratios. The 8%-lanthanum doped PLZT films were prepared with different Zr/Ti ratios on platinized silicon substrates by chemical solution deposition. The pure perovskite phase with a cubic structure in PLZT films was obtained. Films with Zr/Ti: 52/48 had the optimal electrical properties. The relaxor PLZT (8/52/48) is high energy storage density and high energy efficiency that is for capacitor applications.

Tong et al. [12] studied the effects of La contents and substrate strain on the structural, ferroelectric, and dielectric properties of PLZT thin films. The dielectric and ferroelectric properties of PLZT (La = 0, 3, and 10 mol%) thin films deposited on Pt/Si strongly depend on the La-dopant contents. The lattice parameters, grain sizes, and remanent polarization (P_r) of PLZT films decreased as increasing in La contents.

Trivijitkasem et al. [13] characterized Lead Lanthanum Zirconate Titanate (PLZT) ceramics sintered at various temperatures. The remanent polarization (P_r) and coercive field (E_c) decreased when increasing sintering temperature. The sintering behavior and the amount of La_2O_3 doped in PLZT were observed by microstructure. Grains were bigger at the higher sintering temperature and less La^{3+} dopants. Ferroelectric, dielectric and piezoelectric dependence of amount lanthanum content and sintering temperature were studied. The $Pb_{0.95}$ $La_{0.05}(Zr_{0.54}Ti_{0.46})O_3$ ceramics sintered at 1200 ^{o}C was the optimum condition of ferroelectric, dielectric and piezoelectric properties.

Rauls et al. [14] showed the effect of temperature on the large field electromechanical response of relaxor ferroelectric (8/65/35) PLZT. The strain hysteresis loops acquired from butterfly loop below the Curie temperature is independent of electrostrictive coefficient while electric displacement hysteresis loops changed shape from open to linear as the temperature was increased.

Sun et al. [15] showed that thickness has no obvious effect on the phase transition process of (AFE) thick films $Pb_{0\cdot94}La_{0.04}(Zr_{0.98}Ti_{0.02})O_3$ (PLZT4/98/2) with different thicknesses deposited on $Pt(111)/TiO_2/SiO_2/Si(100)$ substrates. However, the dielectric constant was decreased as the film thickness increased.

CHAPTER 3

METRODOLOGY

This chapter illustrates the raw materials, equipment, PLZT tape processing and the characterization of PLZT properties.

3.1 Materials

3.1.1 PLZT powder ($Pb_{0.1}La_{0.9}Zr_{0.35}Ti_{0.65}O_3$)

3.1.2 Solvent (Deionized water)

3.1.3 Binder

3.1.4 Dispersant

3.1.5 Plasticizer

3.1.6 Defoamer

3.2 Laboratory Equipment

3.2.1 Beaker size 50 ml and size 150 ml.

3.2.2 Dropper

3.2.3 Spatula

3.2.4 Mesh

3.2.5 YSZ Ball (yttrium-stabilized zirconia)

3.2.6 Magnetic bar

3.2.7 Plastic bottle size 250 ml.

3.2.8 Carrier tape

3.2.9 Hand cast

3.2.10 Tweezers

3.2.11 Adhesive tape

3.2.12 Cutting tools

3.2.13 Crucibles

3.2.14 Ceramic plates

3.2.15 Gloves

3.2.16 Mask

3.2.17 Plastic bag

3.2.18 Plastic box

3.2.19 Pot mill

3.3 Instruments

3.3.1 Digital Scale

3.3.2 Ball Mill

3.3.3 Magnetic stirrer

3.3.4 Hight tepemperature furnace

3.3.5 X-Ray Diffractometer (XRD) model PANanlytical X Pert PRO at National Metal and Materials Technology Center (MTEC)

3.3.6 Field Emission Scanning Electron Microscope (FE-SEM) ZIESS SUPRA 40 at Magnecomp Precision Technology PCL (MPT)

3.3.7 PalladiumElectrod Sputtering model Quarum 150 R ES at Hutchinson Technology Operations (Thailand) Co.,Ltd (HTO

3.3.8 Dielectric Measurememt (LCR meter) model (A4980 Agilent) at Department of Chemistry, Faculty of Science, King Mongkul's Institute Technology Ladkrabang (KMITL)

3.4 PLZT Tape Fabrication

In the process of PLZT tape fabrication, there are three main steps: PLZT slurry preparation, PLZT tape casting, and sintering. During the dielectric characterization, the

PLZT tape was too brittle. Therefore, the PLZT tape must be stacked before sintering. The PLZT tape fabrication is as follows.

3.4.1 PLZT Slurry Preparation

3.4.1.1 Weigh PLZT powder, DI water, binder, dispersant and YSZ balls and put them into a plastic bottle and insert the plastic bottle in pot mill. The organic system composes of binder, plasticizer, dispersant and defoamer (27 wt.%). The details are shown in Table 3-1.

3.4.1.2 Mix everything by using ball mill for 5 h.

3.4.1.3 After Ball mill for 5 h, PLZT slurry was poured into a beaker by using mesh to separate the YSZ balls from PLZT ball mill.

3.4.1.4 Put the magnetic bar into slurry, stir the slurry and then add binder, plasticizer and defoamer while slurry was stirred.

Table 2 PLZT Slurry composition prepared for tape casting[18]

PLZT slurry composition	Weight %
1. PLZT Powder	55.9
2. Di-ionized water	17.1
3. Binder	24.7
4. Dispersant	1.9
5. Plasticizer	0.2
6. Deformer	0.2

3.4.2 PLZT Tape Casting

3.4.2.1 Place carrier tape on the flat area and use adhesive tapes to fix the carrier tape on the table.

3.4.2.2 Place the hand cast on the carrier tape and pour the PLZT slurry in hand cast. There are five different thicknesses of hand casts: 350, 450, 1000, 1250 and 1500 μm. After that, gently move the hand cast through the carrier tape. The PLZT green tape on the carrier tape was obtained.

3.4.2.3 Dry the PLZT green tape under room temperature at least for 24 h.

Figure 15 shows the whole process of PLZT tape casting process.

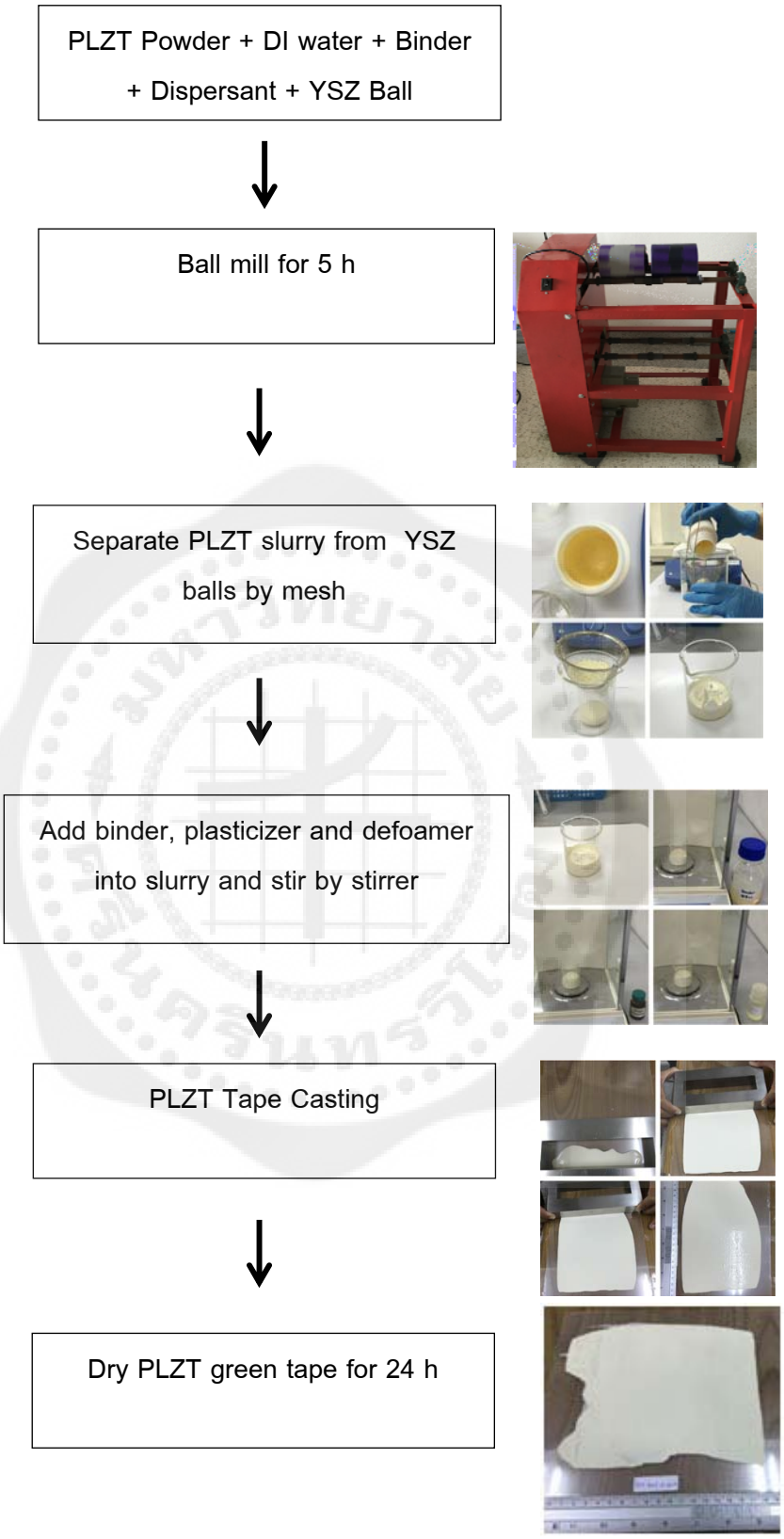


Figure 15 PLZT Green tape preparation steps

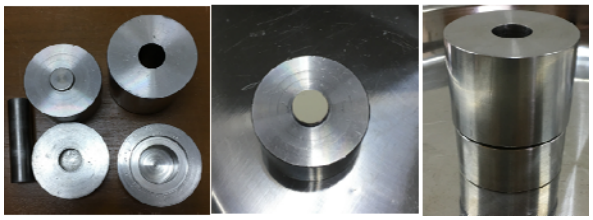
3.4.3 Hydraulic pressure for performing several thicknesses

The PLZT green tape after casing was brittle and fragile. The tape was not able to be characterized the dielectric properties. Therefore, PLZT sheet was punched and then stacked for 4 and 5 layers depend on the desired thickness. The experimental details was as follows.

3.4.3.1 The PLZT green tape was punched out to circle shapes with diameter 13 mm.

3.4.3.2 The PLZT green tapes were stacked in the die and baked at 90^{o}C for 30 min.

3.4.3.3 After baking the stacked green tape in the die, the die was pressed by hydraulic pressure with 2 ton for 12 s.

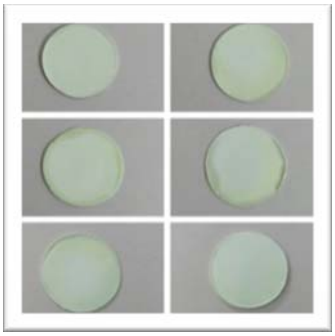


90 °C for 30 min

5000 N for 6 s

20000 N for 12 S

1100 °C for 30 min



PLZT tapes

Figure 16 Stacking PLZT sheet step for dielectric test

The six PLZT thicknesses with 1400, 2150, 2850, 3350, 4250 and 4950 μm of each decreased organic system were prepared by stacking PLZT sheets with hydraulic press. The details of stacked PLZT from single PLZT sheet are shown in Appendix Table A1.

3.4.4 Sintering Process

The PLZT green tapes were placed in the crucible filling with PLZT powder to compensate the lead loss of PLZT phase. The ceramic plate was placed on top of the green tape to prevent green tape from bending as shown in Figure 16. The green tapes were sintered in the furnace at 1100°C for 30 min. Figure 18 and Figure 19 show the sintering profile with ramp up rate and cooling rate and high temperature furnace, respectively.

Figure 17 PLZT tape placed in the crucible for sintering at 1100 °C for 30 min

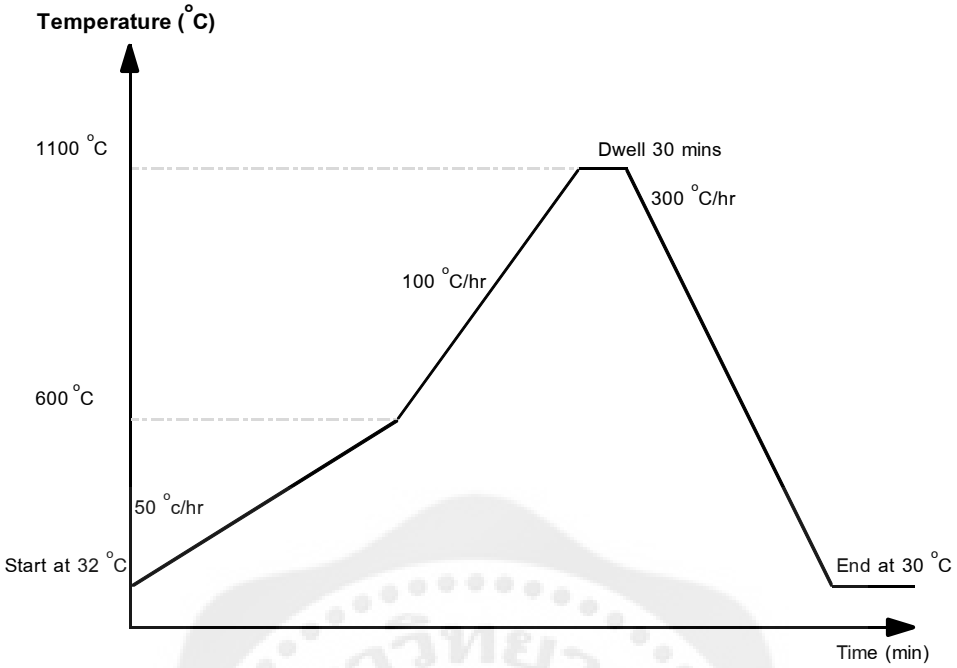


Figure 18 Sintering profile

Figure 19 High temperature furnace for sintering PLZT tape

3.5 PLZT Characterizations

3.5.1 Structural Characterization

The structure and orientation of PLZT tape were characterized by a high power X-ray diffractometer (XRD) (PANanlytical X Pert PRO) at National Metal and Materials Technology Center (MTEC). The high power source of diffractometer is Cu K_α radiation. PLZT tape was scanned with 2θ from 20 to 60 degrees with 50 kV, 300 mA, 0.02°/step and 0.5 sec/step. A schematic of X-ray diffraction geometry is shown in FIGURE 20 and FIGURE 21.

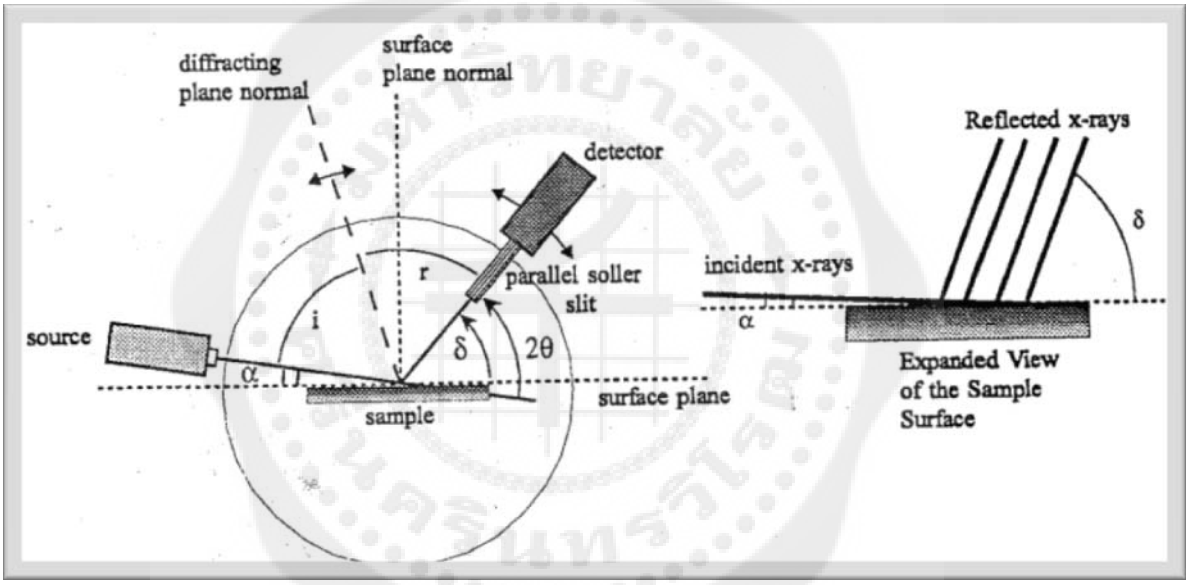


Figure Schematic XRD technique [3]

Figure 20 XRD Instrument (PANanlytical X Pert PRO)

3.5.2 Surface Microstructural and Thickness Characterization

Field Emission Scanning Electron Microscope, FE-SEM is the most widely used instrument to characterize the surface microstructure and composition of materials. In this study, PLZT film was characterized by FE-SEM model ZIESS SUPRA 40 at Magnecomp Precision Technology PCL (MPT) as shown in FIGURE 22 A secondary electron detector was used to provide surface microstructural information with 15 keV of accelerating voltage. Before characterization, the PLZT samples were coated with palladium (Pd) to provide an electrical conductive layer. The grain size was determined from the FE-SEM micrographs by using FE-SEM software. The chemical composition of PLZT was analyzed by Energy Dispersive X-Ray Spectrometer, EDS (Oxfords).

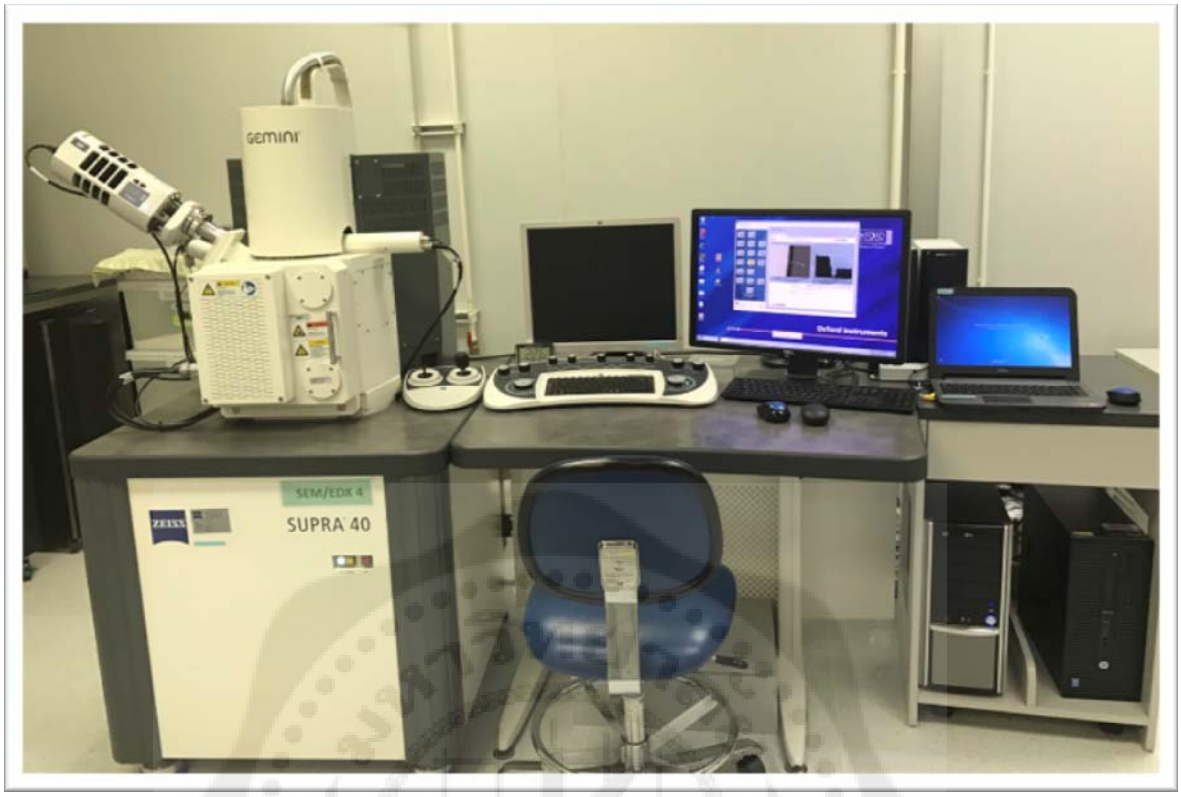
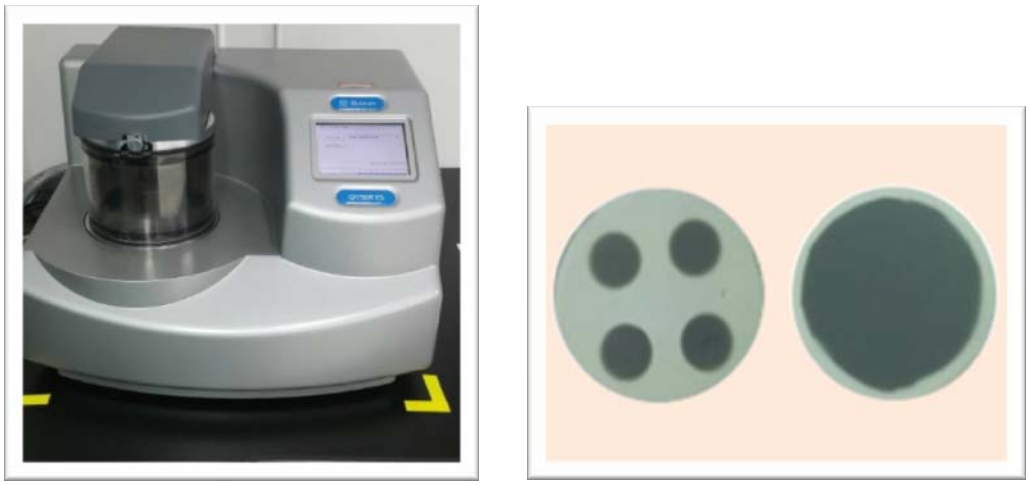


Figure 21 FE-SEM/ EDS Instrument (ZIESS SUPRA 40)

3.5.3 Dielectric Constant Characterization

Prior to the capacitance measurement, the top and bottom palladium electrodes were coated by sputtering (Quarum 150 R ES) at Hutchinson Technology Operations (Thailand) Co.,Ltd (HTO as shown in FIGURE 21 (a) and FIGURE 9 (b) shows the pattern of electrode. The Pd top electrodes with 3 mm diameter were deposited through a plastic shadow mask.



(a) (b)

Figure 22 (a) Sputtering (Quarum 150 R ES and (b) left: top electrode and right: bottom electrode

The capacitances were measured by using LCR Meter model (A4980 Agilent) at Department of Chemistry, Faculty of Science, King Mongkul's Institute Technology Ladkrabang (KMITL) as shown in FIGURE 23. Low field measurements were made under resonance frequency at 20 - 100,000 kHz with 30 mV oscillation voltages. . The dielectric permittivity was calculated as shown in EQUATION 3-1.

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d}$$ EQUATION 3–1[1]

Where

C = capacitance (F)

ε_0 = permittivity of a vacuum or the permittivity of free space = 8.854 x 10^{-12} F/m

ε_r = relative permittivity of the material or dielectric constant

A = area (m^2)

d = distance between plates (m)

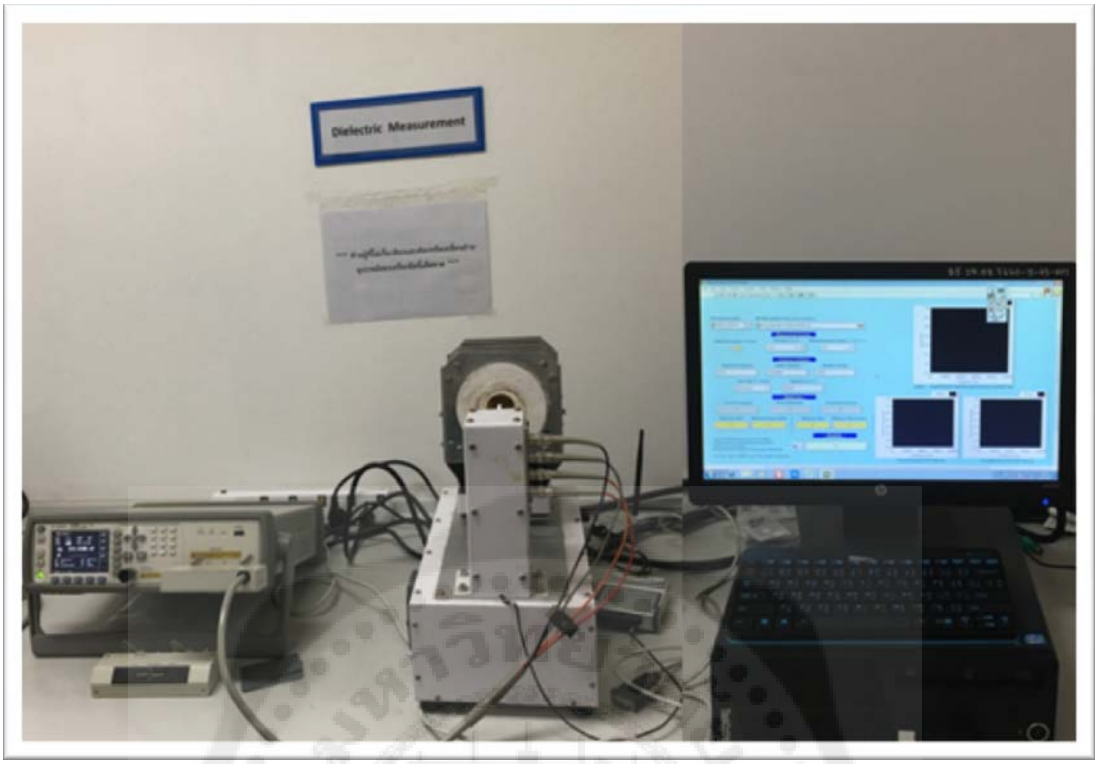


Figure 23 LCR meter model (A4980 Agilent)

CHAPTER 4

RESULTS AND DISCUSSIONS

This chapter describes the results of PZT tape casting fabrication, microstructrural and thickness characterization, and dielectric properties.

4.1 Tape Casting of PLZT Fabrication

The organic system is composed of deionized-water, binder, plasticizer, defoamer, and dispersant. The organic system was decreased for 10-40 wt.%. The PLZT can be fabricated by decreasing the organic system for 10-30 wt. % of PLZT slurry. The details of PLZT slurry are as follows.

- PLZT slurry without decreasing of organic system : the high viscosity PLZT slurry was observed.
- PLZT with decreasing organic system for 10 wt. %: the viscosity of PLZT slurry was slightly decreased. After casting, the small porosities were found on the surface of PLZT green tape. The process of casting with this condition is easier than the PLZT slurry without decreasing of organic system.
- PLZT with decreasing organic system for 20 wt. %: the vicostity of PLZT slurry was moderate. Small porosities were found on the surface of PLZT tape after fabricated of tape casting.
- PLZT with decreasing organic system for 30 wt. %: the viscosity of PLZT slurry was low. Large porosities were found after fabrication that might cause from slurry shrinkage during fabricating.
- PLZT with decreasing organic system for 40 wt. %: it is obvious to see that the viscosity was very low and the shrinkage occured during tape casting. PLZT slurry could not be casted with this condition.

Therefore, the reduction of organic system for 10-30 wt.% of PLZT slurry can be fabricated by tape casting but there are more bubbles on PLZT tape with decreasing the amount of organic system. TABLE 3 summarizes the result of PLZT slurry and PLZT

fabrication with decreasing the organic system for 10-40 wt.%. The green PLZT tapes after fabrication of each condition were shown in FIGURE 4-1.

Table 3 Summary of PLZT tape casting with decreasing organic system for 10-40 wt. %.

PLZT with decreasing organic system (wt.%)	**PLZT tape casting**	**Observations**
0	Achieved	- High viscosity.
10	Achieved	- Moderate viscosity..
20	Achieved	- Moderate viscosity. - Small porosity on surface of green tape.
30	Achieved	- Low viscosity. - Large porosity on surface of green tape
40	Not achieved	- Very low viscosity - Shrinkage during fabricated of tape casting.

(a) (b) (c)

(d) (e)

Figure 24 PLZT green tapes with decreasing organic system (a) PLZT tape without decreasing organic system (b) PLZT tape with decreasing organic system for 10 wt.% (c) PLZT tape with decreasing organic system for 20 wt.% (d) PLZT tape with decreasing organic system for 30 wt.% and (e) PLZT tape with decreasing organic system for 40 wt.%

4.2 Structural Characterization

The structural and orientation of PLZT tapes were characterized by X-Ray diffraction PANalytical X' Pert PRO, XRD. The high power source of diffractometer is Cu K_α radiation. PLZT tape was scanned with 2θ from 20 to 60 degrees with 50 kV, 300 mA, 0.02°/step and 0.5 sec/step. The crystal structure of PLZT tape is perovskite polycrystalline with (100), (110), (111), (200), (210) and (211), which are matched to PLZT in JCPDS file number 29-776[21]. The structure of PLZT tape with decreasing the amount of organic system shows similar

microstructure to PLZT tape without decreasing the amount of organic system. FIGURE 25 shows the XRD pattrn of PLZT tape.

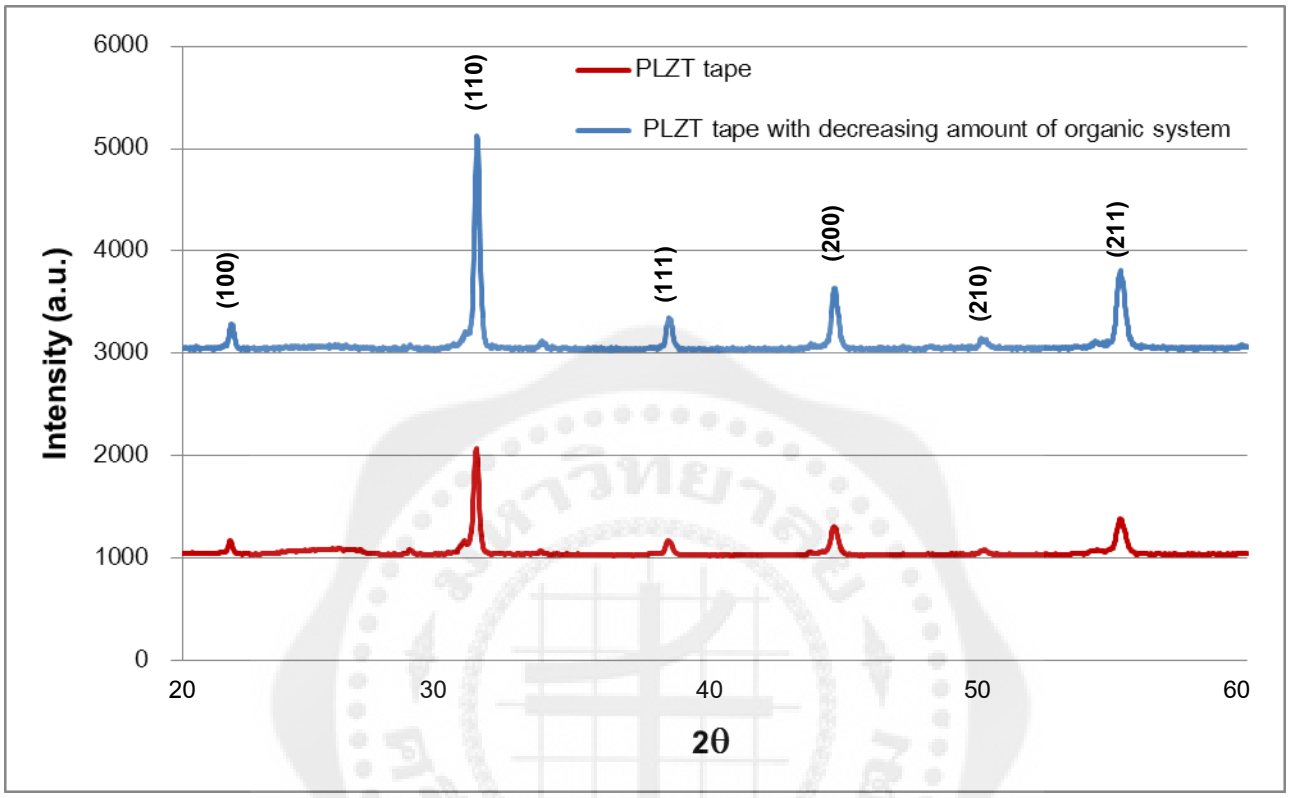


Figure 25 X-ray diffraction pattern of PLZT tape with decreasing amount of organic system

4.3 Surface morphology and Thickness Characterization

The surface morphology of PLZT tape was characterized using Field Emission Scanning Electron Microscopy (FE-SEM) after sintering at 1100°C for 30 min. The thickness of PLZT tapes were 40 μm to 245 μm depend on the thickness of hand cast.

The porosity on the surface of PLZT tape was observed. The more decrease of organics system, the more the porosity was observed. The average grain size of PLZT tape was about 1 μm. FIGURE 26 shows the surface of PLZT tape after sintering at 1100°C for 30 min.

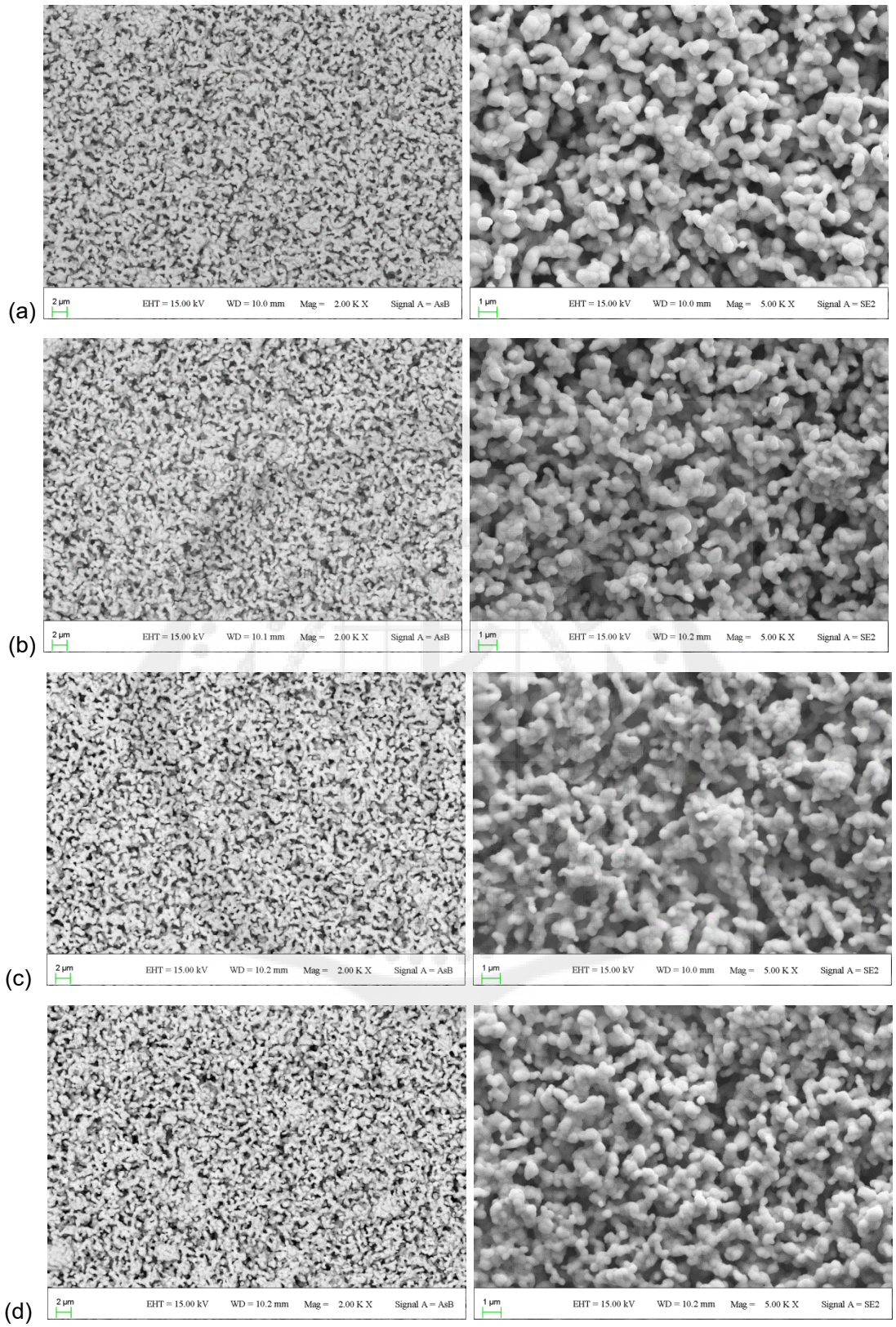
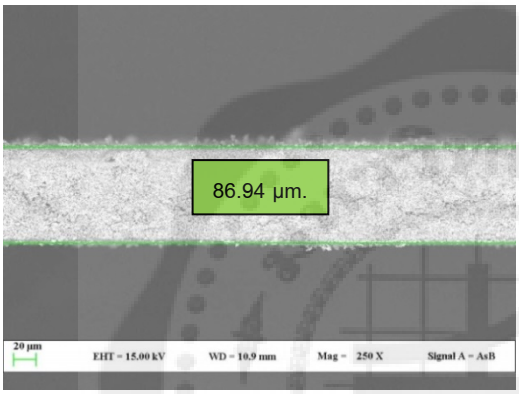
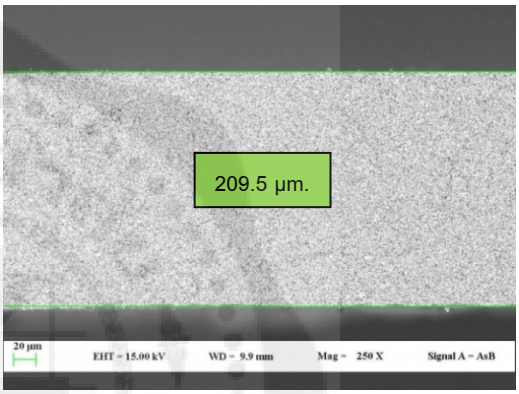


Figure 26 Surface morphology of single sheet of PLZT tape (a) PLZT tape without decreasing organic system (b) PLZT tape with decreasing organic system for 10 wt.% (c) PLZT tape with decreasing organic system for 20 wt.% and (d) PLZT tape with decreasing organic system for 30 wt.%

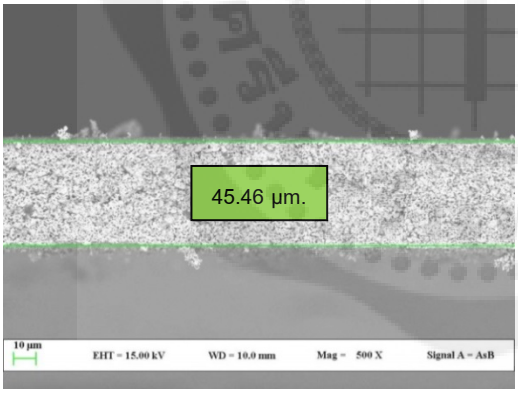
The thickness of PLZT tapes after sintering at 1100^{o}C for 30 min was determined by Field Emission Scanning Electron Microscope technique (FESEM). The thickness of PLZT tapes depends on the hand cast thickness. In this study, the thickness of hand cast were 350, 450, 1000, 1250 and 1500 µm. The thickness of PLZT tapes after sintering was decreased for 80-90% from the thickness indicated from hand-cast. The thickness of PLZT sheet after sintering ranged from 40 µm to 245 µm as shown in FIGURE 27 TABLE 24 summarizes the thickness of sigle layer of PLZT tape with and without decreasing organic system.

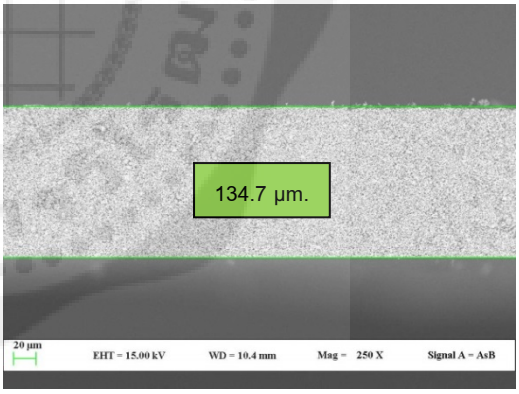
(a)



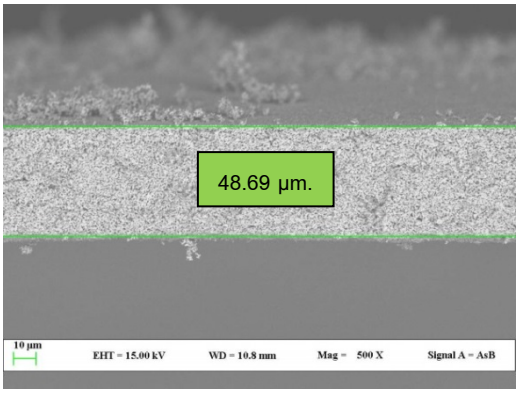


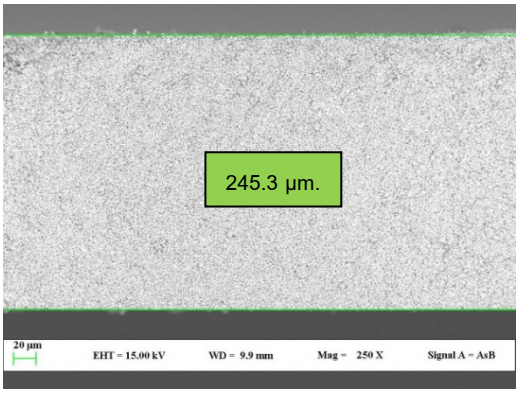
(b)





(c)





(d)

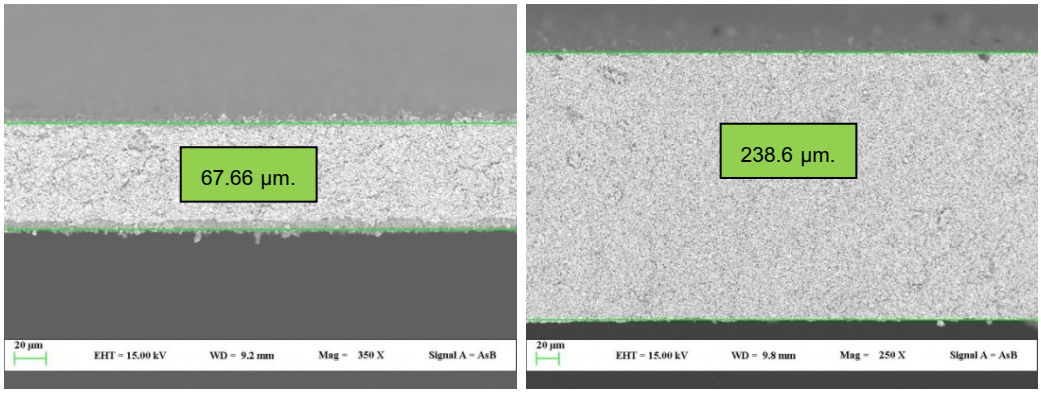


Figure 27 FESEM image for thickness of PLZT tape(a) PLZT tape without decreasing organic system (b) PLZT tape with decreasing organic system for 10 wt.% (c) PLZT tape with decreasing organic system for 20 wt.% and (d) PLZT tape with decreasing organic system for 30 wt.%

Table 4 Summary of PLZT tapes thickness with and without decreasing organic system for 10-30 wt. %

PLZT tape decreasing of organic system (wt.%)	Single layer
	Thickness before sinter 350-1500 µm
0	75-210 µm
10	40-135 µm
20	45-245 µm
30	70-240 µm

The single layer of PLZT tape is brittle and the dielectric property was not able to be characterized. Thereore, PLZT tapes were stacked for 4-5 layers and baked at 90^{o}C for 30 min. After that the stacked tapes were pressed by hydraulic pressure at 5000 N for 6 s and 20000 N

for 12 s. The stacked PLZT tapes have more strength and dielectric property was able to be characterized.

The surface of stacked PLZT tapes were characterized. The results show that the tapes without decreasing organic system has less porosity on the surface while the PLZT tapes with decreasing organic system for 10-20 wt.% of organic system has more porosity spread on the surface of stacked PLZT . The average grain size was about 1 μm after sintering at 1100^{o}C for 30 min shown as FIGURE 28-29. FIGURE 28 and FIGURE 29 show the stacked PLZT tapes by hydraulic pressure at 5000 N for 6 s and 20000 N for 12 s, respectively.

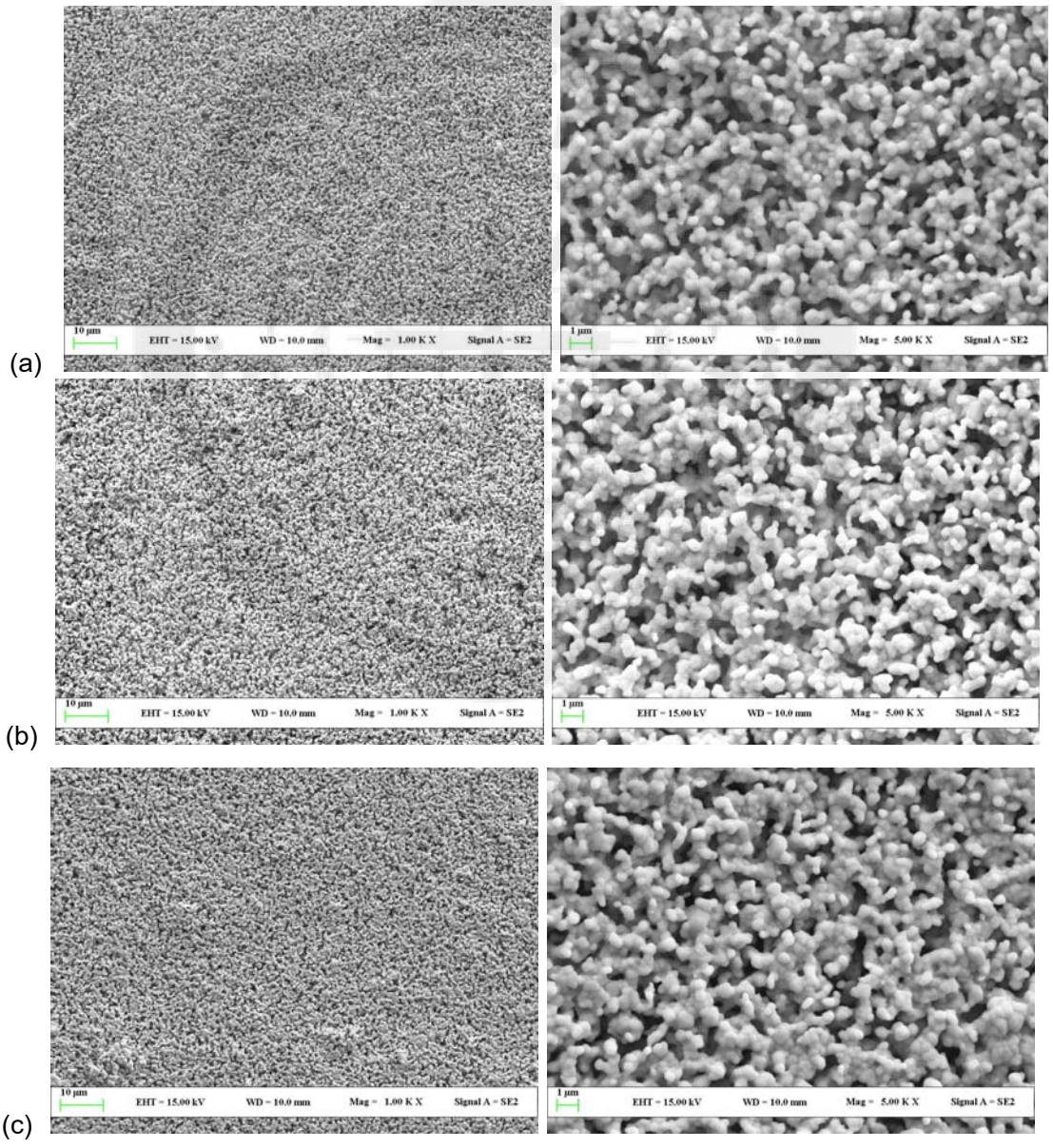


Figure 28 FESEM image of surface morphology of stacked PLZT tapes by 5000 N for 6 s (a) PLZT tape without decreasing organic system (b) PLZT tape with decreasing organic system for 10 wt.% and (c) PLZT tape with decreasing organic system for 20 wt.%

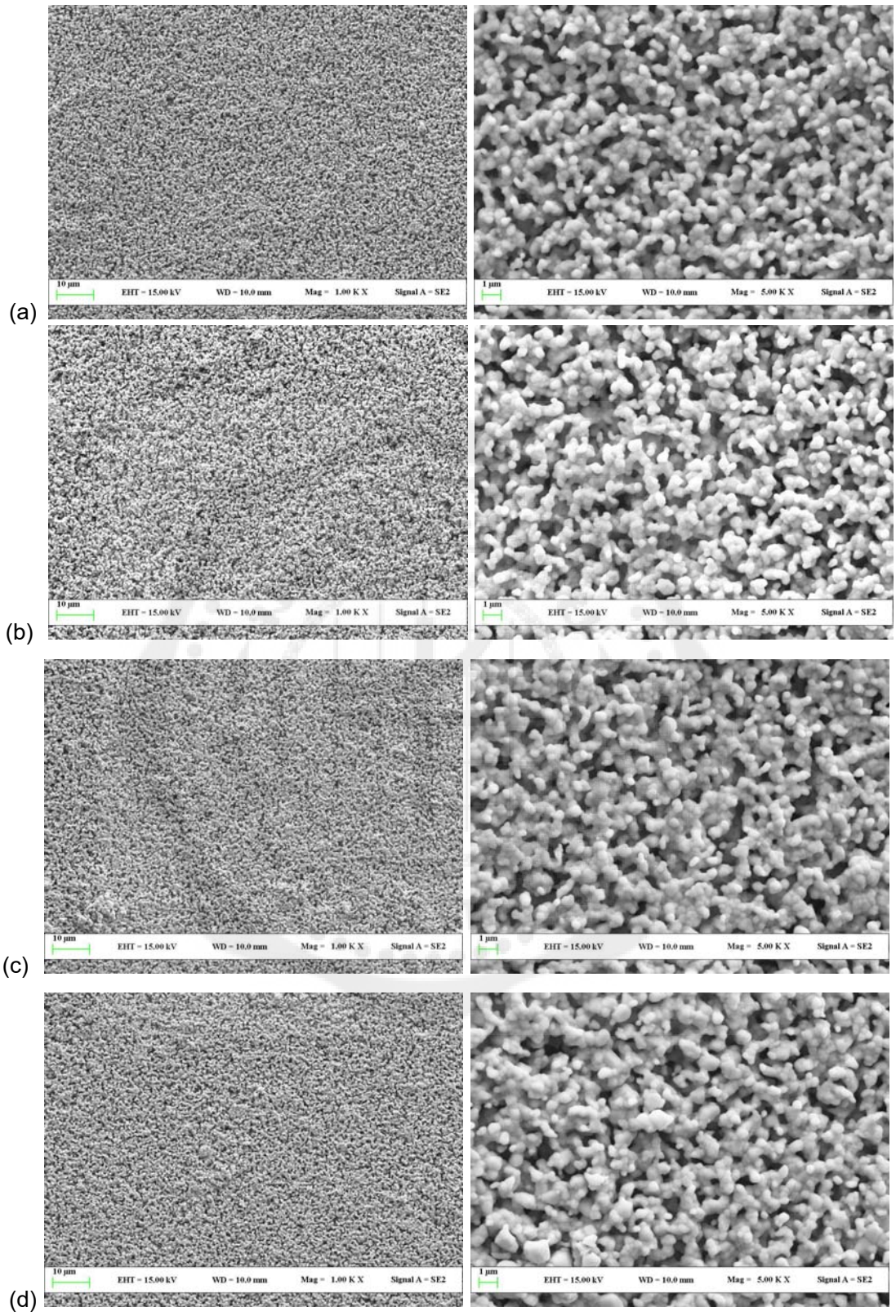


Figure 29 FESEM image of surface morphology of stacked PLZT tapes by 20000 N for 12 s (a) PLZT tape without decreasing organic system (b) PLZT tape with decreasing organic system for 10 wt.% (c) PLZT tape with decreasing organic system for 20 wt.% and (d)

The thickness of stacked PLZT tapes with 5000 N for 6 s before sintering were 1400, 2250, 2850, 3350, 4250 and 4950 μm. The thickness of stacked PLZT tape with 20000 N for 12 s before sintering was 2500 μm. However, the thickess of stacked PLZT tapes after sintering at 1100^{o}C for 30 min was decreased and ranged from 240 μm to 680 μm. The thickness of PLZT tape was determined by Field Emission Scanning Electron Microscope (FE-SEM) shown as FIGURE 4-7-4.9 for stacked PLZT tapes with 5000 N for 6 s. TABLE 5 summarizes the thickness of stacked PLZT tape with and without decreasing organic system by hydraulic pressure 5000 N for 6 s and FIGURE 33 shows the thickness of stacked PLZT tapes with and without decreasing organic system by hydraulic pressure 20000 N for 12 s.

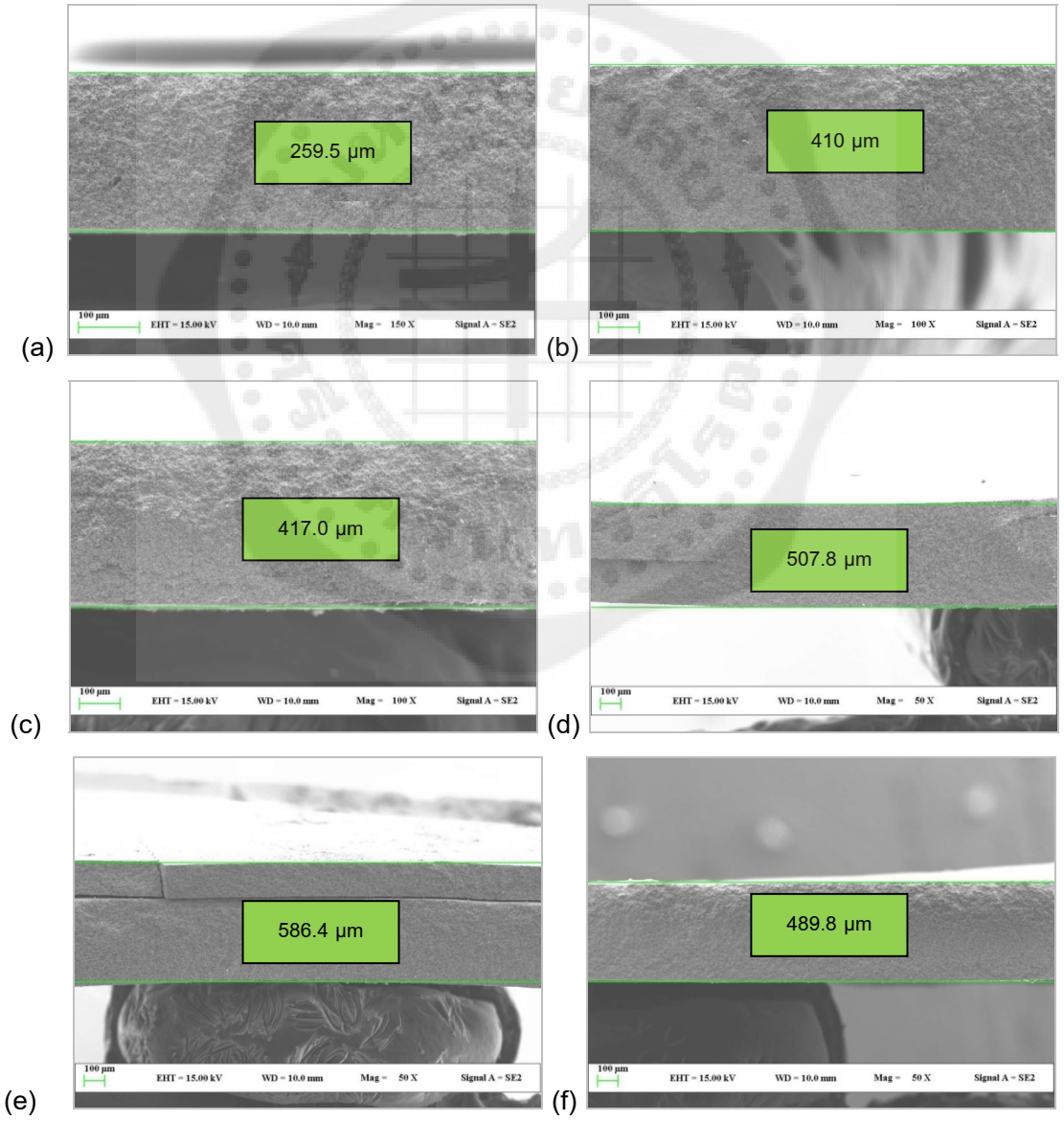


Figure 30 FESEM image of thickness of stacked PLZT tapes with 5000 N for 6 s without decreasing of organic system (a) 259.9 μm (b) 410.0 μm (c) 407.8 μm (d) 507.8 μm (e) 489.8 μm and (f) 586.4 μm

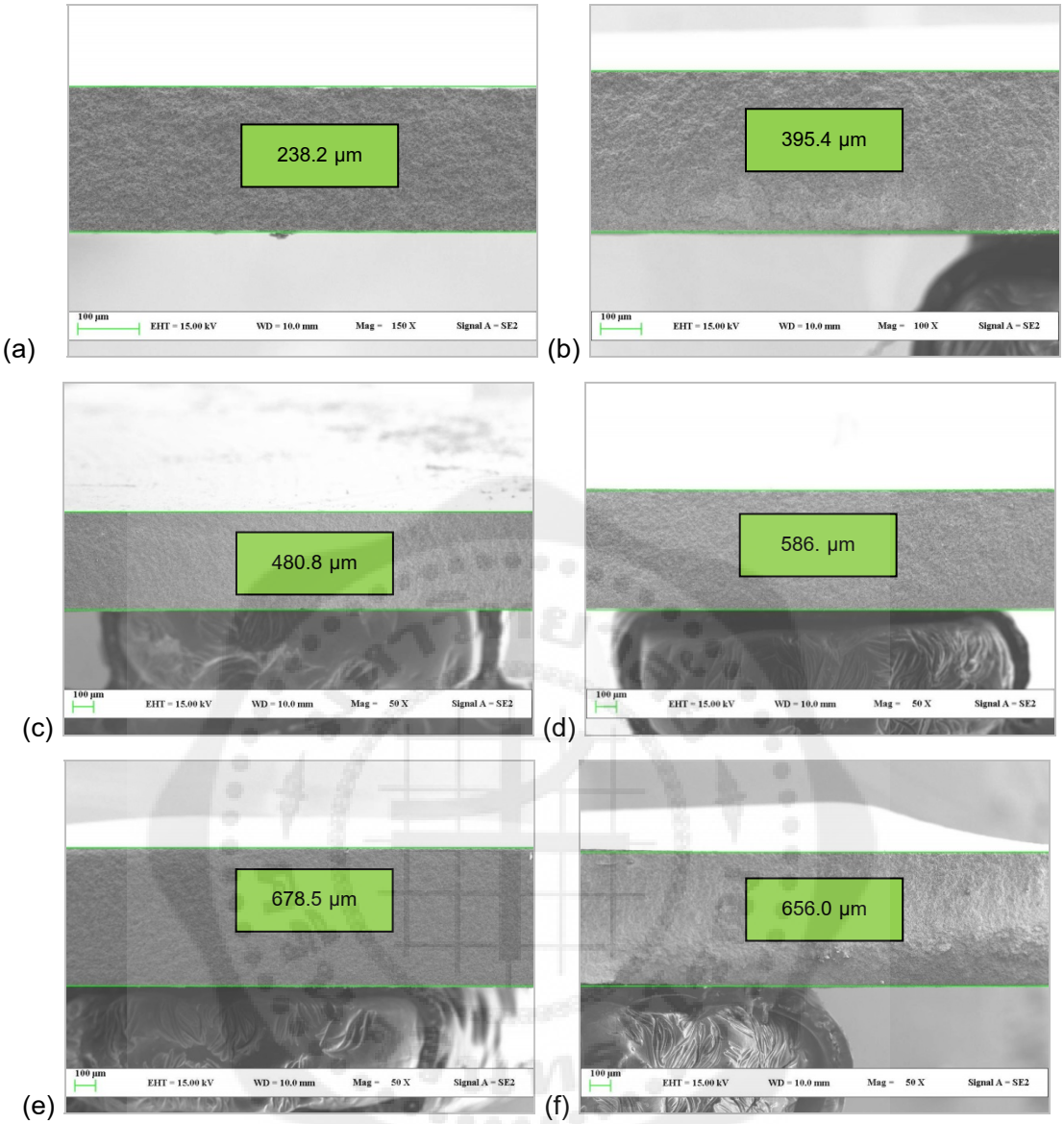


Figure 31 FESEM image of thickness of stacked PLZT tapes with 5000 N for 6 s with decreasing organic system for 10 wt. % with thickness (a) 238.2 µm (b) 395.4 µm (c) 480.8 µm (d) 586.4 µm (e) 656.0 µm and (f) 678.5 µm

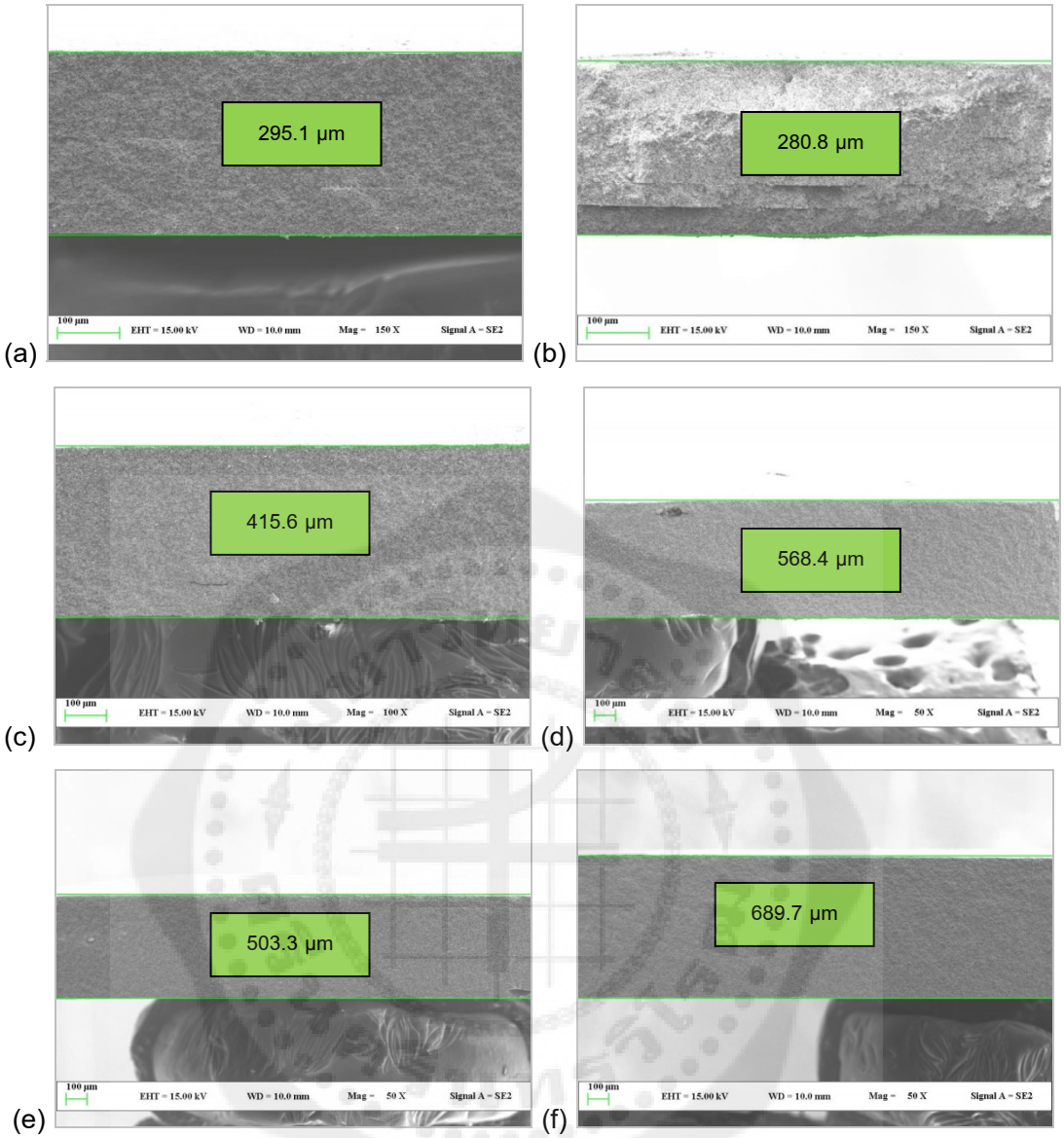


Figure 32 FESEM image of thickness of stacked PLZT tapes with 5000 N for 6 s with decreasing organic system for 20 wt. % with thickness (a) 295.1 µm (b) 280.8 µm (c) 415.6 µm (d) 568.4 µm (e) 503.3 µm and (f) 689.7 µm

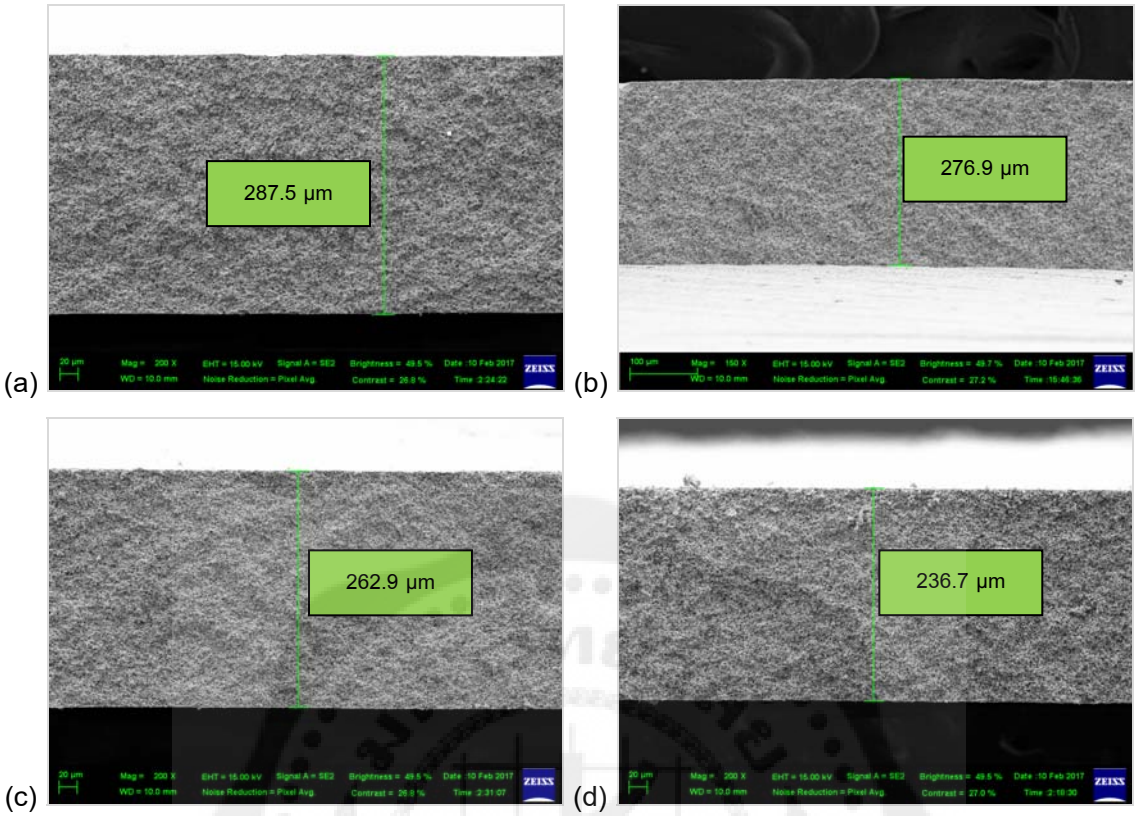


Figure 33 FESEM image of stacked PLZT tapes with 20000 N for 12 s (a) PLZT tape without decreasing organic system : 287.5 µm (b) PLZT tape decreasing organic system for 10 wt.%: 276.9 µm (c) PLZT decreasing organic system for 20 wt.%: 262.9 µm and (d) PLZT decreasing organic system for 30 wt.%: 236.7 µm

Table 5 Summary of thickness of stacked with 5000 N for 6 s of PLZT tapes with and without decreasing for 10-20 wt. %

PLZT tape decreasing of organic system (wt.%)	Multilayer PLZT
	Thickness before sinter 1400- 4950 µm
0	260-590 µm
10	240-680 µm
20	280-690 µm

4.4 Dielectric Constant Characterization

The dielectric properties were characterized by LCR Meter (A4980 Agilent) with frequency ranged from 20 Hz to 100,000 Hz.

4.4.1 Dielectric Constant of PLZT Thickness Variation

PLZT tapes were stacked 4-5 layers by hydraulic pressure at 5000 N for 6 s and then sintered at 1100 ^{o}C for 30 min. PLZT tapes with different thicknesses were obtained and the dielectric properties were characterized.

The dielectric constant of PLZT tapes revealed that the thicker PLZT tapes showed less dielectric constant as shown in FIGURE 34. As frequency increased, the dielectric constant decreased.

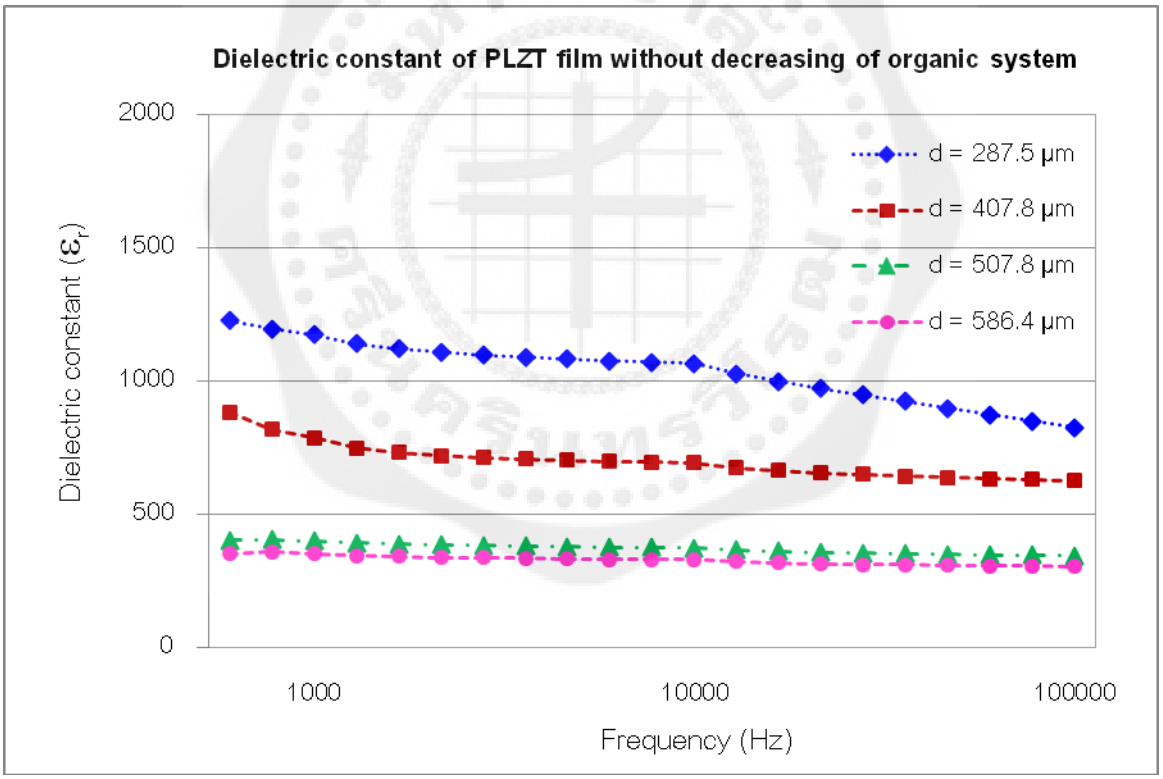


Figure 34 Dielectric constant dependence of frequency at different thickness of PLZT tapes without decreasing of organic system

The dielectric loss of PLZT tapes as a function of frequency without decreasing organic system at different thickness are shown in FIGURE 34. The dielectric loss shows comparable level for thickness that varied from 6.9-10 % at 1 kHz.

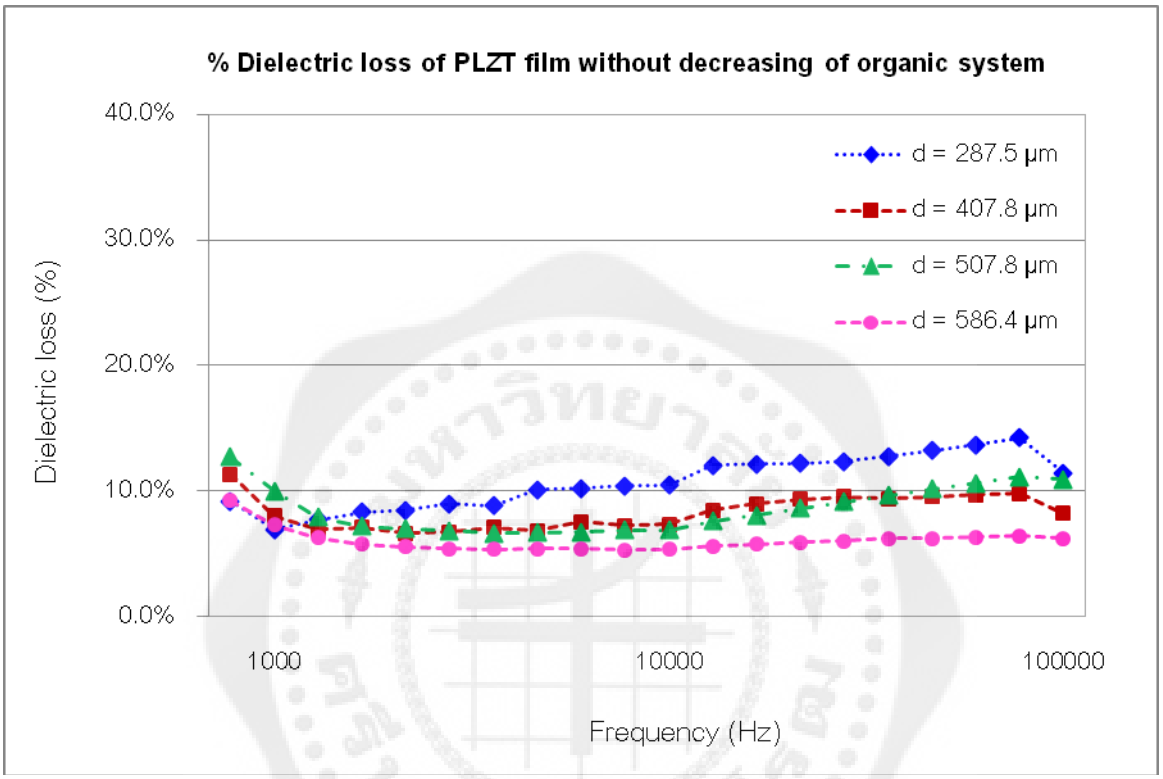


Figure 35 Dielectric loss dependence of frequency of different thickness of PLZT tapes without decreasing organic system

The dielectric constant, capacitance, and loss of PLZT tapes at 1 kHz without decreasing organic system at different thickness are shown in TABLE 6. The thiner PLZT tape shows higher dielectric constant and capacitance values.

Table 6 Dielectric constant, capacitance and loss of PLZT tapes without decreasing organic system

PLZT tape thickness (μm)	ε_r (1 KHz)	Capacitance (pF) (1 kHz)	Loss (%)
287.5	1173	267.2	6.9
407.8	786	135.3	7.9
507.8	399	49.5	10
586.4	351	37.4	7.3

FIGURE 36 shows the dielectric constant as a function of frequency of PLZT tapes with decreasing organic system for 10 wt.%. It is found that the dielectric constant is lower than the PLZT tapes without decreasing organic system.

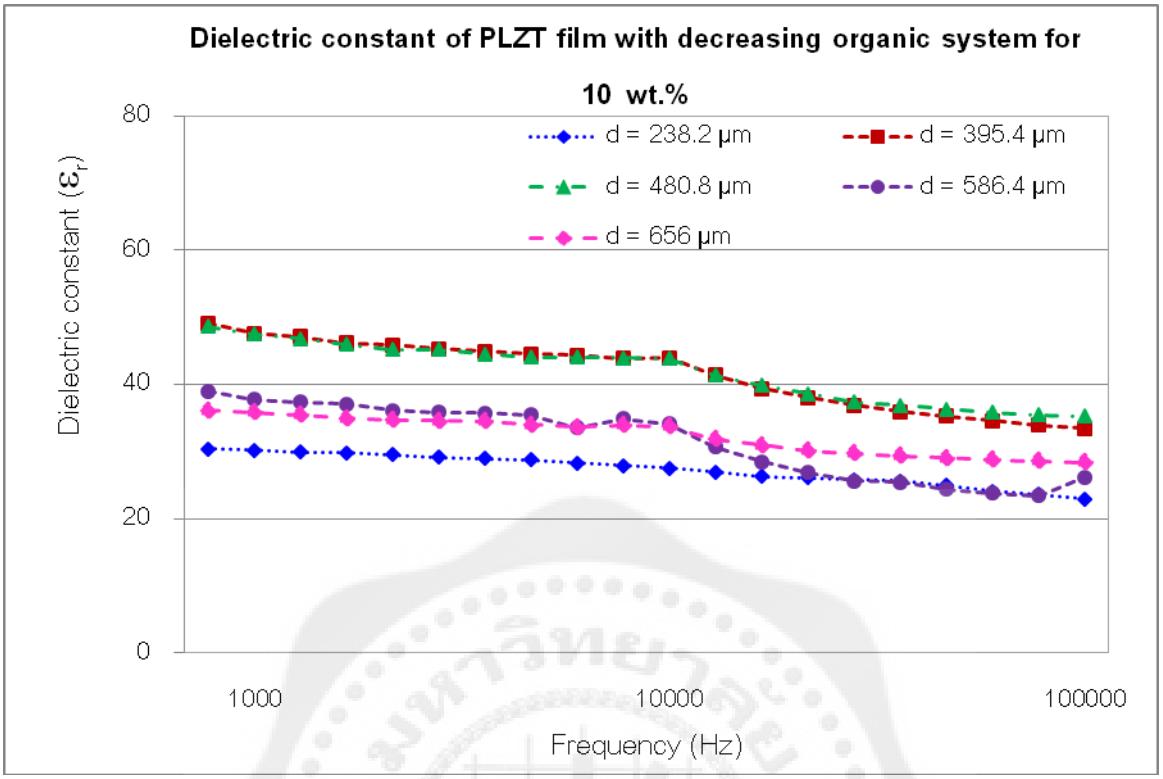


Figure 36 Dielectric constant as a function of frequency of PLZT tapes with decreasing organic system for 10 wt. %

The dielectric constant of PLZT tapes with decreasing organic system for 10 wt.% with 395.4 and 480.8 µm thick revealed comparable level as 47- 48 while PLZT tape 586.4 and 656.0 µm thick show comparable level as 36-38. However, the dielectric constant for PLZT with decreasing organic system for 10 wt.% varied from 30-48.

The dielectric loss of PLZT tapes as a function of frequency with decreasing organic system for 10 wt.% different thickness are shown in FIGURE 36. The dielectric loss of PLZT tapes with decreasing organic system for 10 wt.% with 238.2 and 395.4 µm thick revealed increasing trend after frequency at 10 kHz. The dielectric loss of PLZT tapes with decreasing organic system for 10 wt.% varied from 4.3 -5.4 % at 1 kHz.

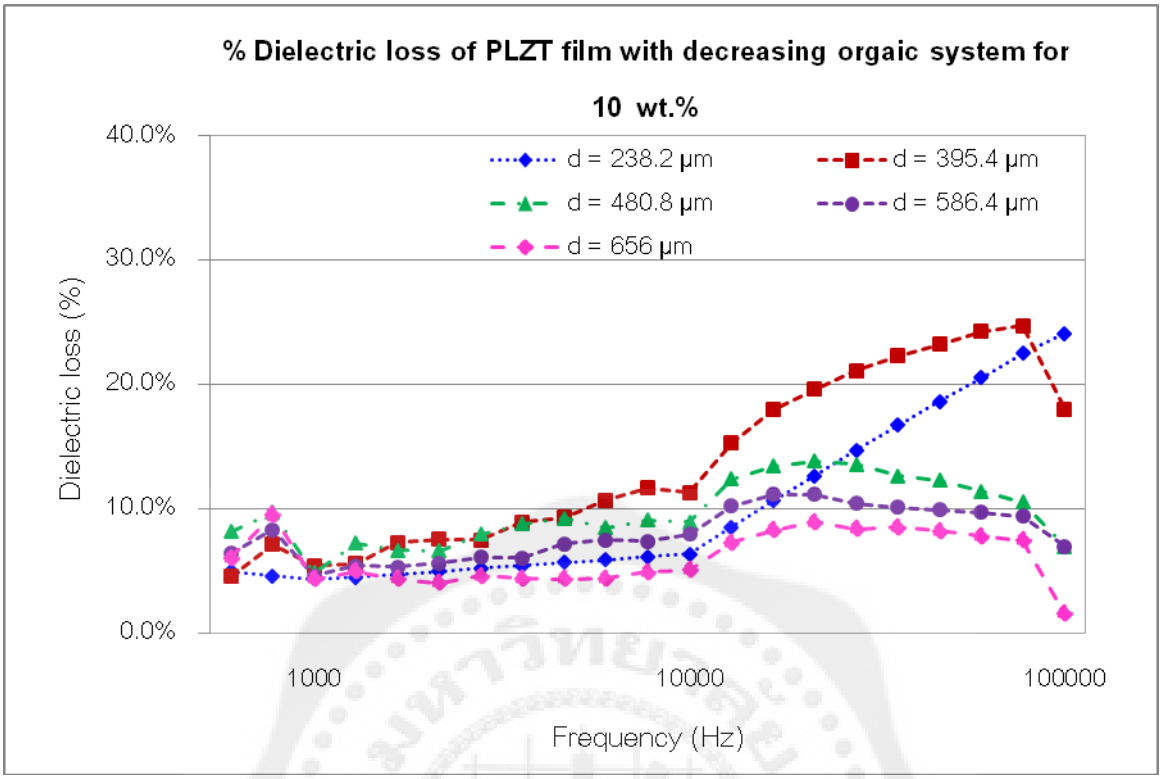


Figure 37 Dielectric loss as a function of frequency of PLZT tapes with decreasing organic system for 10 wt. %

The dielectric constant, capacitance, and loss of PLZT tapes with decreasing organic system for 10 wt.% at different thickness are shown in TABLE 7.

Table 7 Dielectric constant, capacitance, and loss of PLZT tapes with decreasing organic system for 10 wt. %

PLZT tape Thickness (µm)	ε_r (1 KHz)	Capacitance (pF) (1 kHz)	Loss (%)
238.2	30	7.9	4.3
395.4	48	7.5	5.4
480.8	47	6.2	4.8
586.4	38	4.0	4.6
656.0	36	3.4	4.3

FIGURE 38 shows the dielectric constant as a function of frequency of PLZT tapes with decreasing organic system for 20 wt.%. The thicker PLZT tapes show less dielectric constant and capacitance values.

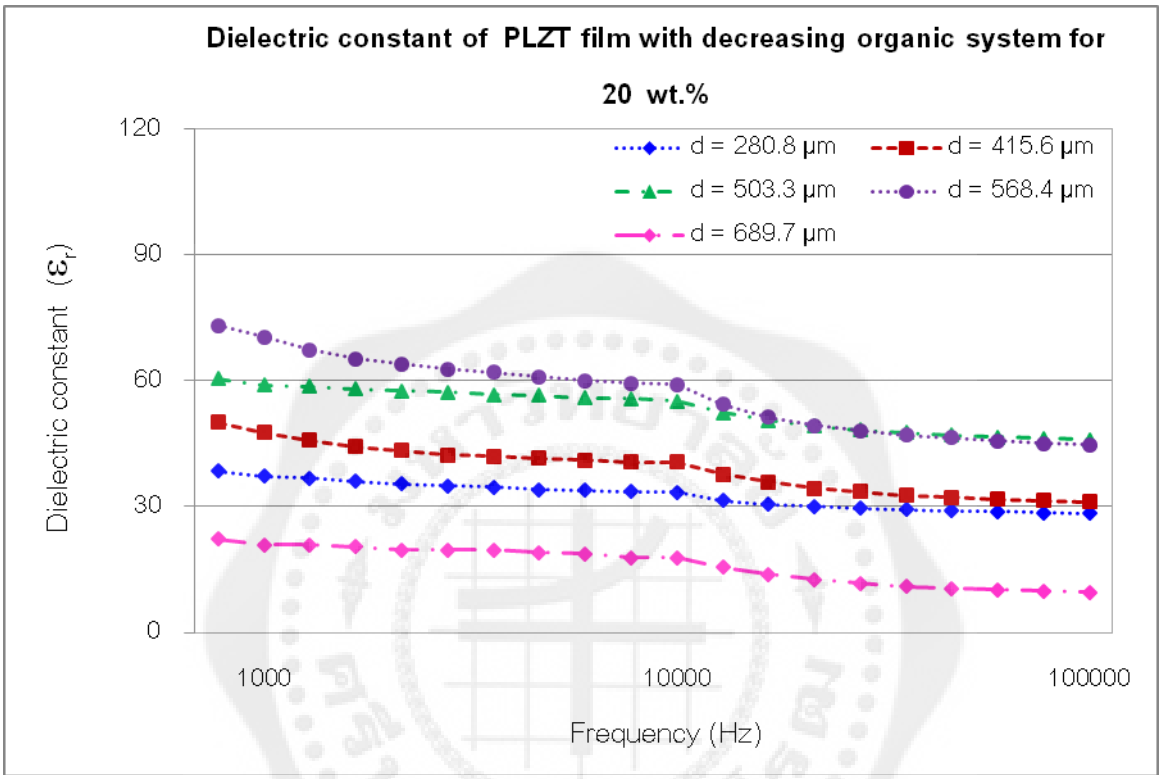


Figure 38 Dielectric constant as a function of frequency of PLZT tapes with decreasing organic system for 20 wt. %

The dielectric constant of PLZT tapes with decreasing organic system for 20 wt.% with 568.4 µm thick revealed the highest level as 70 while PLZT tape with 689.7 µm thick shows the lowest level as 21. However, the dielectric constant for PLZT with decreasing for 20 wt.% varied from 21-70.

The dielectric loss of PLZT tapes as a function of frequency with decreasing organic system for 20 wt.% at different thickness are shown in FIGURE 38. The dielectric loss of PLZT tapes with decreasing organic system for 20 wt.% with 689.7 µm thick revealed increasing trend

after frequency at 1 kHz. The dielectric loss of PLZT tapes with decreasing organic system for 20 wt.% varied from 2.6-6.3 % at 1 kHz.

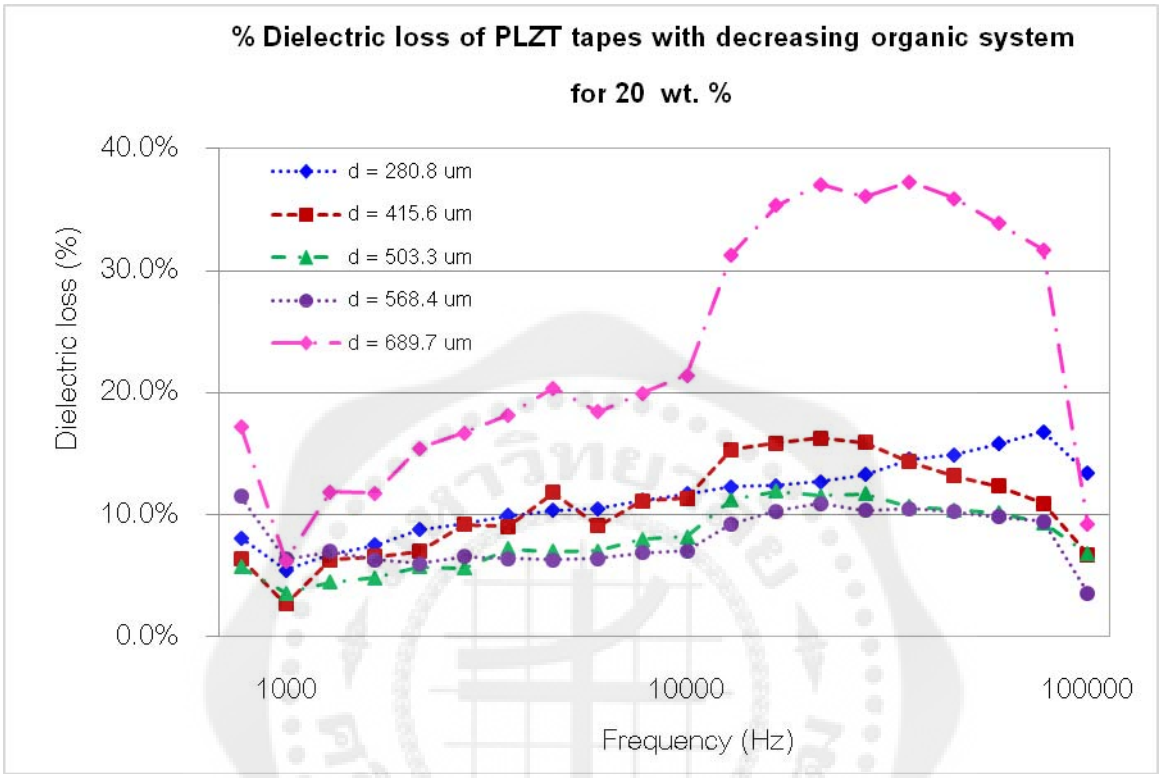


Figure 39 Dielectric loss as a function of frequency of PLZT tapes with decreasing organic system for 20 wt. %

The dielectric constant, capacitance, and loss for PLZT tapes with decreasing organic system for 20 wt.% at different thickness are shown in TABLE 8.

Table 8 Dielectric constant, capacitance, and loss of PLZT tape with decreasing organic system for 20 wt. %

PLZT tape Thickness (μm)	ε_r (1 KHz)	Capacitance (pF) (1 kHz)	Loss (%)
280.8	37	8.3	5.4
415.6	48	7.2	2.6
503.3	59	7.3	3.5
568.4	70	7.8	6.3
689.7	21	1.9	6.2

4.4.2 Dielectric Constant of Organic System Variation

PLZT tapes with 240 - 290 μm thick of different organic system pressed by hydraulic pressure 20000 N for 12 s were characterized.

PLZT tapes were stacked 2 layers by hydraulic pressure at 20000 N for 12 s and then sintered at 1100 $^{\circ}$C for 30 min. PLZT tapes with different organic system were obtained and the dielectric properties were characterized.

The dielectric constant of PLZT tapes as a function of frequency revealed that PLZT tapes without decreasing organic system shows higher dielectric constant than PLZT tapes with decreasing organic system for 10-30 wt. % as shown in FIGURE 40. As frequency increased, the dielectric constant decreased.

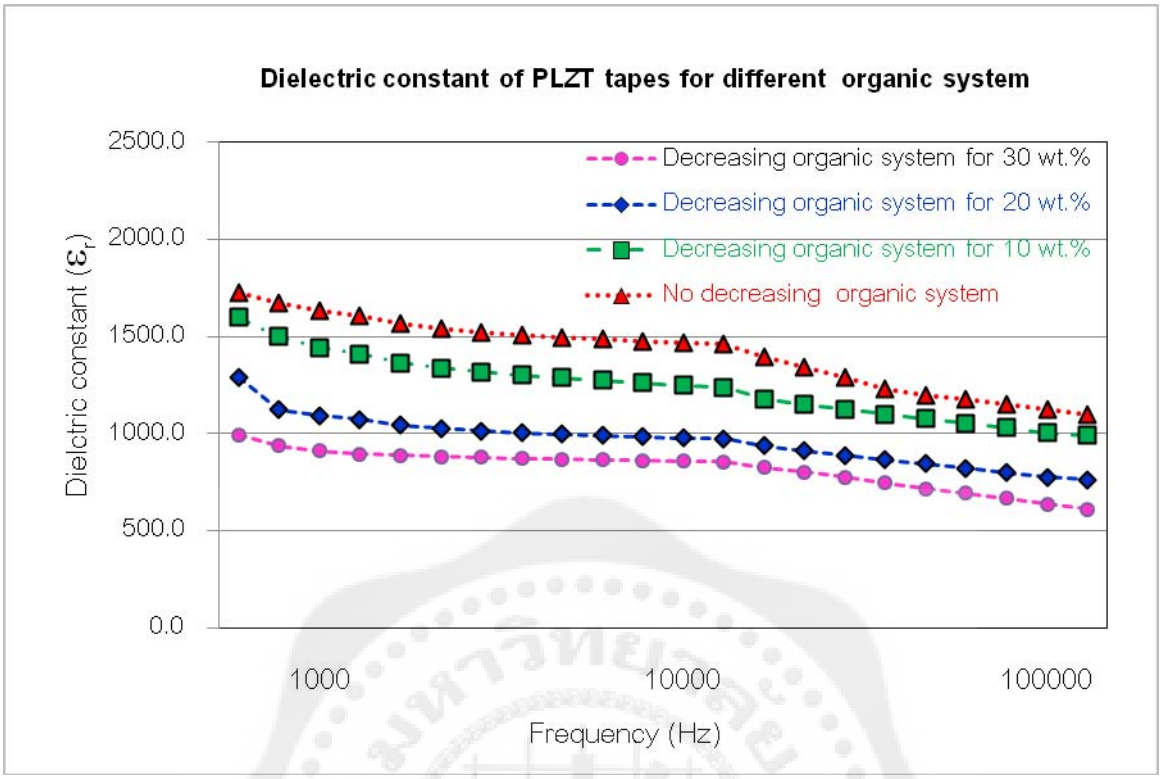


Figure 40 Dielectric constant as a function of frequency of PLZT tapes with different organic system

The dielectric constant of PLZT tape without decreasing of organic system revealed the highest dielectric constant as 1607 while PLZT tapes with decreasing organic system for 10-30 wt.% varied from 895 – 1359.

The dielectric loss of PLZT tapes as a function of frequency at organic system are shown in FIGURE 41. The dielectric loss of PLZT tapes revealed comparable level but after frequency 10 kHz observed increasing dielectric loss. The dielectric loss of PLZT tapes with different organic system varied from 6.6-9.2 % at 1 kHz.

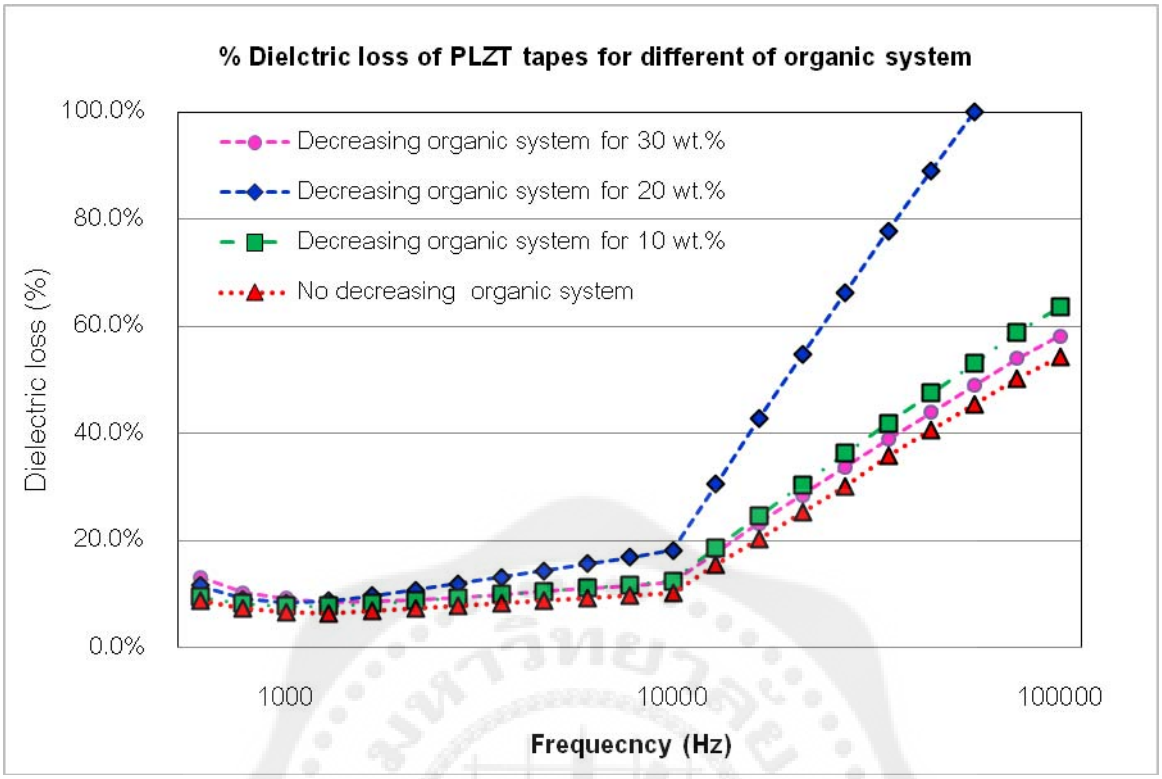


Figure 41 Dielectric loss as a function of frequency of PLZT tapes with different organic system

The dielectric constant, capacitance, and loss of PLZT tapes at 1 kHz different organic system are shown in TABLE 9.

Table 9 Dielectric constant, capacitance, and loss of PLZT tapes for different of organic system

PLZT tapes with decreasing of organic system (wt.%)	ε_r (1 KHz)	Capacitance (pF) (1 kHz)	Loss (%)
0 (d= 287.5 μm)	1607	349.8	6.6
10 (d=276.9 μm)	1359	315.3	7.8
20 (d=262.9 μm)	1072	255.3	8.4
30 (d=238.6 μm)	895	234.9	9.2

CHAPTER 5

CONCLUSIONS

In this studied, the effect of organic system reduction on the fabrication of Lead Zirconate Titanate doped with Lanthanum ($Pb_{0.9}La_{0.1}Zr_{0.35}Ti_{0.65}O_3$, PLZT) PLZT by tape casting was studied. The organic system is composed of binder, plasticizer, dispersant and defoamer. The organic system was decreased for 10-30 wt.%.

The reduction of organic system for 10-30 wt.% of PLZT slurry can be fabricated by tape casting but there were more bubbles on PLZT tape with decreasing the amount of organic system. The crystal structure of PLZT tape was perovskite polycrystalline with (100), (110), (111), (200), (210) and (211). The microstructure of PLZT tapes has uniform grain shapes and grain sizes with and without decreasing organic system. More porosities were observed on PLZT tapes with decreasing organic system. PLZT tapes have an average grain size about 1 μm over the PLZT tape surface.

The thickness of PLZT tapes were 40 μm to 245 μm depend on the thickness of hand cast. The single layer of PLZT tape was brittle, So, the hydraulic pressure was employed to increase the strength of PLZT tapes. The stacked PLZT tapes have more strength and dielectric property was able to be characterized. The thickness of stacked PLZT tapes were 240 μm to 245 μm.

The dielectric constant, capacitance, and loss of PLZT tapes at 1 kHz without decreasing organic system at different thickness of thinner PLZT tapes show higher dielectric constant and capacitance values than thicker PLZT tapes. The dielectric constant as a function of frequency of PLZT tapes with decreasing organic system for 10-20 wt.%. was lower than the PLZT tapes without decreasing organic system. The dielectric constant of PLZT tapes with decreasing organic system for 10-20 wt.% varied from 20-70. The lower values may be caused from more porosities on PLZT tapes with decreasing organic system. The dielectric loss of PLZT tapes with decreasing organic system for 10-20 wt.% with different thickness revealed increasing trend after frequency at 10 kHz that varied from 2.6-6.3 %.

The dielectric constant of PLZT tapes of PLZT tapes without decreasing organic system was 1607 while PLZT with decreasing organic system for 10-30 wt. % varied from 895-1359. As frequency increased, the dielectric constant decreased.TABLE 10 summarizes the results of PLZT tape casting, PLZT grain size, dielectric constant, and loss of PLZT tapes for each conditons.

Table 10 Summary physical and dielectric properties of PLZT film with decreasing organic system for 10-40 wt. %

PLZT decreasing of organic system (wt.%)	PLZT tape casting	PLZT grain size (μm)	Dielectric constant (ε_r)	Loss (%)
0	Yes	1	1607	6.6
10	Yes	1	1359	7.8
20	Yes	1	1072	8.4
30	Yes	1	895	9.2
40	No	1	-	-

Future Work

In this study the problems during tape casting process are the porosity that was observed on surface of PLZT green sheet with decreasing for organic system. Therefore, it is important to decrease the bubbles in the slurry preparation step of the PLZT slurry resulting in prorosity on the PLZT tapes. Moreover, PLZT tapes after sintering process was brittle. The process would be de-air the PLZT slurry. It is interesting in studying the parameters that affect the strength of PLZT tapes after sintering process because PLZT green tape after sintering was brittle. If the PLZT tapes have more strength, the piezoelectric property would be enhanced. Moeover, the physical properties (density and percent shrinkage) and mechanical property (hardness) should be investigated.

Also, the changes in dopant ratio and the alternative dopants would be studied. The ratio and alternative dopants would enhance the piezoelectric property of PLZT tapes.

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APPENDIX

APPENDIX A

Stacking PLZT sheets with hydraulic press

APPENDIX A

Stacking PLZT sheets with hydraulic press

The six PLZT thicknesses with 1400, 2150, 2850, 3350, 4250 and 4950 μm were prepared by stacking PLZT sheets with hydraulic press. The details of stacked PLZT from single PLZT sheet are shown in Appendix Table A1.

TABLE A1: The details of stacked PLZT from single PLZT sheet

Thickness before sintering (μm)	Stacked PLZT Sheets
1400	350 μm (4 layers)
2150	350 μm (1 layer) + 1450 μm (4 layers)
2850	450 μm (3 layers) + 1500 μm (1 layer)
3350	350 μm (2 layers) + 450 μm (3 layers) + 1500 μm (1 layer)
4250	350 μm (1 layer) + 450 μm (2 layers) + 1500 μm (2 layers)
4950	350 μm (2 layers) + 1250 μm (1 layer) + 1500 μm (2 layers)

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