Chapter 2

Literature review

2.1 Basics of ferroelectrics

2.1.1 Introduction

Internal structures of materials are interesting for an understanding on the concept of ferroelectric and piezoelectric materials. The crystals can be divided to 7 basic crystal systems and they can be separated to 32 point groups by symmetry of unit cell in which they are shown in Fig. 2.1 and Table 2.1. From 32 point groups, 11 point groups are centrosymmetric and 21 point groups are noncentrosymmetric. All centrosymmetrics can not posses polar properties or spontaneous polarization. Of the remaining 21 noncentrosymmetric, 20 point groups have one or more polar axes and they are the piezoelectric, whereas another one (432 point group) does not show this property. In a piezoelectric type, 10 point groups are the pyroelectric; spontaneously polarized under temperature conditions and a subgroup of this is the ferroelectric. Hence, all single crystals and successfully poled ceramics, which show ferroelectric behavior are pyroelectric, but not vice versa.[2,24,25]

2.1.2 Ferroelectricity and related properties (piezoelectricity and dielectric)

2.1.2.1 Ferroelectricity

Ferroelectric materials are a subgroup of pyroelectric and piezoelectric materials. They have a specific property called "ferroelectricity' which was discovered in 1921. The materials in this group are spontaneously polarized like pyroelectrics. Furthermore, they can be demonstrated re-orienting of the polarization whereas pyroelecric materials can not show this phenomenon. All ferroelecrtic materials have a transition temperature called the Curie point (T_c). At a temperature $T < T_c$ the crystal is ferroelectric, while $T > T_c$ it does not exhibit ferroelectricity. A nonpolar phase above T_c is the so-called paraelectric phase.[1,2,38]
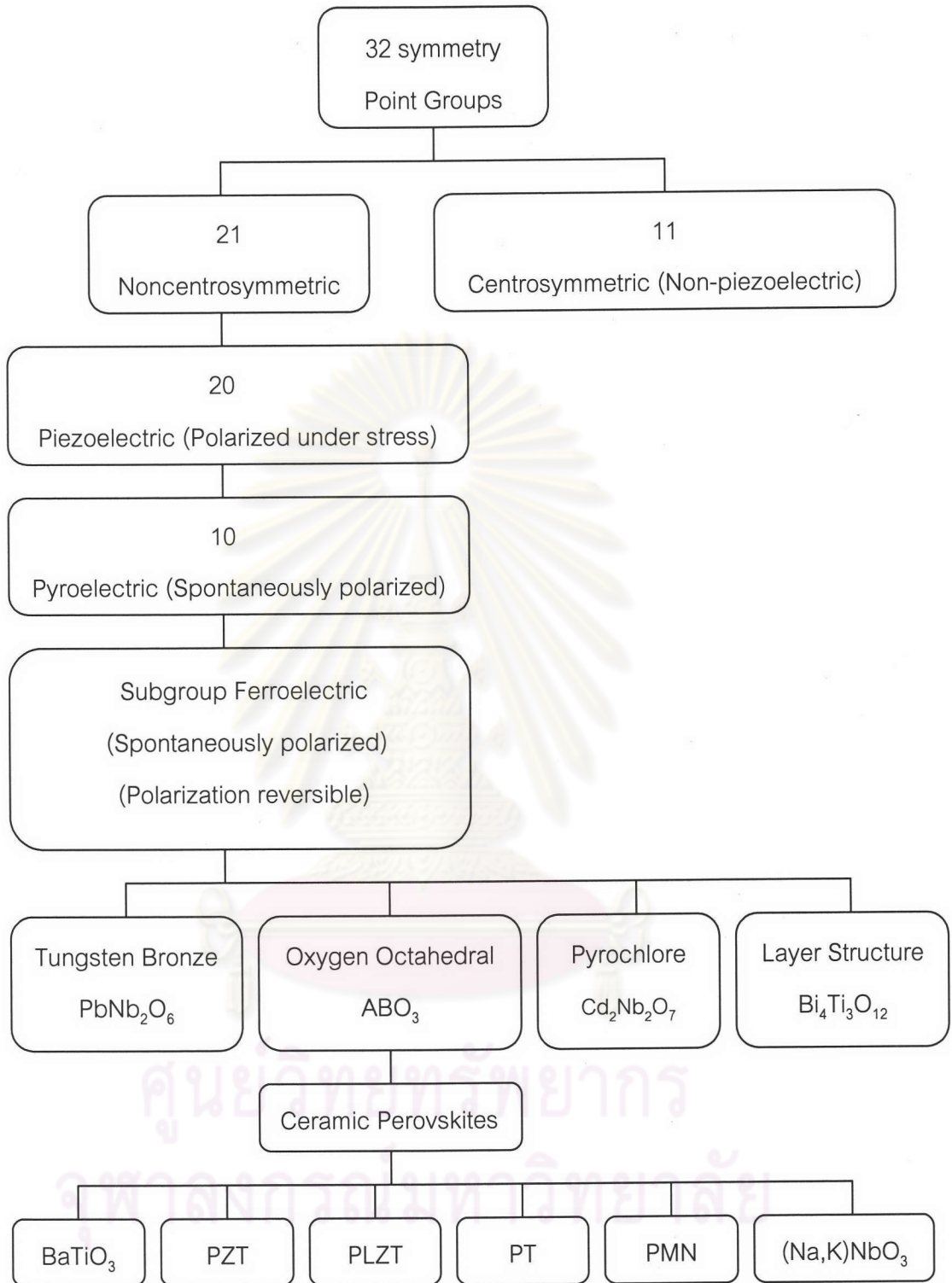
Fig. 2.1 Interrelationship of piezoelectric and subgroups on the basis of symmetry.[1]

Table 2.1 The 32 crystal point groups.[24]

Optical axes	Crystal class	Centrosymmetric point group		Noncentrosymmetric point group			
				Polar		Nonpolar	
Biaxial	Triclinic	$\bar{1}$		1		none	
	Monoclinic	2 or m		2	m	none	
	Orthorhombic	mmm		mm2		222	
Uniaxial	Tetragonal	4 or m	4 or mmm	4	4mm	$\bar{4}$	$\bar{4}$2m	22
	Trigonal	$\bar{3}$	$\bar{3}$m	3	3m		32
	Hexagonal	6 or m	6 or mmm	6	6mm	$\bar{6}$	$\bar{6}$m2	622
Optically isotropic	Cubic	m3	m3m	none		432	$\bar{3}$m	23
Total number		11 groups		10 groups		11 groups	

The reversible polarization is an essential property for ferroelectric materials. A hysteresis loop for polarization in an alternating field is used for explanation this property. A typical ferroelectric hysteresis loop is shown in Fig. 2.2. Different domains in these materials are initially reversible dipoles after an alternating electric field is applied. At the highest field strength, the increase of polarization for given increase in the field
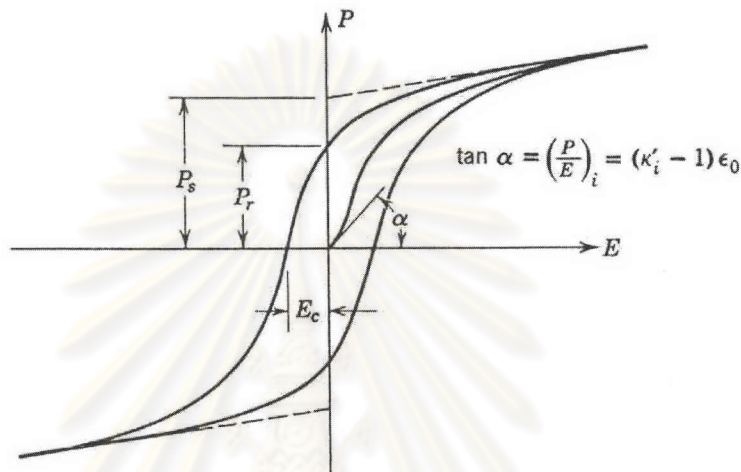

$$\tan \alpha = \left(\frac{P}{E}\right)_i = (\kappa_i' - 1)\epsilon_0$$

Fig. 2.2 A typical ferroelectric hysteresis loop.[7]

strength, corresponding to polarization saturation, P_s, having all the domains of like orientation aligned in the direction of the electric field. P_s is the spontaneous polarization with all the dipoles aligned in parallel. When the electric field is cut off (E=0), the polarization does not return to zero but it remains a finite value called the remanent polarization, P_r. The polarization go back to zero if an oppositely directed field is applied. This field is known as the coercive field, E_c.

2.1.2.2 Piezoelectricity

Piezoelectricity is the property of a crystal to exhibit electric polarity when applied stress. The name "Piezo" is derived from the Greek, which means "to press".[1] The piezoelectricity was discovered in 1880 by Jacques and Pierre Curie during their systematic study of the effect of pressure on the generation of electrical charge by crystals, such as quartz, zincblende, and tourmaline.[1,3,24] The piezoelectricity has 2 effects in piezoelectric crystals, in general, and in ferroelectric ceramics, in particular. They are the direct effect and the converse effect. The direct effect is shown as

electrical charge (polarization) when mechanical stress is applied to these materials. On the other hand, the converse effect is associated with mechanical movement generated by the application of an electric field as shown in Fig. 2.3.[36] If we apply an electric potential as shown, a crystal will lengthen because of the attractions of the ions to the poled plates. If we use an ac voltage, the crystal will alternatively expand and contract.[36] These effects are given in equations 2.1 and 2.2.[23]

$$D = dT + \varepsilon^{T}E \text{ (direct effect)} \qquad (2.1)$$

$$S = s^{E}T + dE \text{ (converse effect)} \qquad (2.2)$$

Where D is the dielectric displacement (consider it equal to

polarization)

T is the stress

E is the electric field strength

S is the strain

d is a piezoelectric coefficient

s is the material compliance (inverse of stiffness)

ε is the dielectric constant

In open circuit, g coefficients are used to evaluate piezoelectric materials for their ability to generate large amount of voltage per unit of input stress. The g constant and d constant are relative to the equation as follows:[1]

$$g = d/K\varepsilon_0 \qquad (2.3)$$

Where K is the relative dielectric constant

ε_0 is the permittivity of free space (8.854×10^{-12} F/m)

The piezoelectric coupling factor (e.g., k_{33}, k_{31}, and k_p) is an important property of a piezoelectric material, which is the fraction of electrical energy that can convert into mechanical energy and vice versa. The equation of electromechanical coupling coefficient, k, is illustrated in equations 2.4 (direct effect) and 2.5 (converse effect).[1,8]

$$k^2 = \frac{\text{mechanical energy converted to electrical energy}}{\text{input mechanical energy}} \qquad (2.4)$$

$$k^2 = \frac{\text{electrical energy converted to mechanical energy}}{\text{input electrical energy}} \qquad (2.5)$$

(a)   (b)   (c)
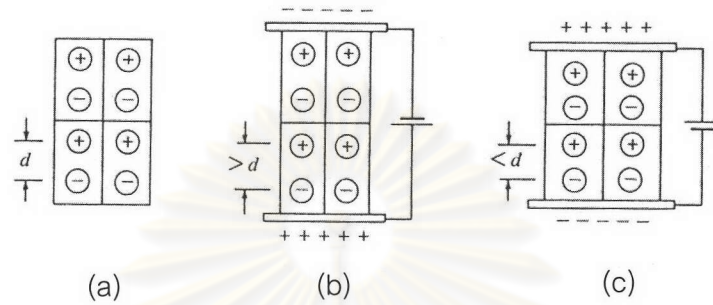
Note: d = distance

Fig. 2.3 (a) piezoelectric material, (b) An electric field induces dimensional expansion, (c) Reverse polarity causes a corresponding contraction. The procedure can be inverted by applying a pressure and obtaining a change in voltage.[36]

2.1.2.3 Dielectric properties

Dielectric materials mean the materials, which permit the passage of the lines of force of an electrostatic field but do not conduct the current. The dielectrics have two functions to perform. One is to act as an insulator and the second is to increase the capacitance of a condenser (capacitor).[37] Typically ferroelectric materials have a high relative dielectric constant (relative permitivity), ε_r.[39]

The relative dielectric permittivity or the dielectric constant, ε_{rij}, is:[8]

$$\varepsilon_{ij} = \varepsilon_0 \varepsilon_{rij} \qquad (2.6)$$

where ε_0 is the dielectric permittivity of vacuum (8.854×10^{-12} Fm^{-1})

ε_{ij} is the dielectric permittivity of material (Fm^{-1})

Otherwise, the dielectric permittivity together with a geometrical factor determines the capacitance of a component as equation 2.7. [8]

$$C = \varepsilon_0 \varepsilon_r^{(n)} A/t \qquad (2.7)$$

where   C   is the capacitance (Farads)

$\varepsilon_r^{(n)}$ is the projected dielectric constant in the direction normal to the plane of the capacitor

A   is the electrode surface of the capacitor

T   is the thickness between the electrodes

The high values of dielectric constants are required for capacitors, whereas low values are used as insulating materials. [37]

The dissipation factors are also important values in dielectric materials. When alternating current provides the voltage needed to maintain the charge on capacitors or any dielectrics, the current leads the voltage by 90 - δ, where the angle δ is called the dielectric-loss angle. [37] If the dielectrics were perfect, the angle δ would be zero and no loss would occur. [37,38] The tangent of the angle δ (tan δ) is known as the dissipation factor. Multiplying tan δ by the dielectric constant (K) expresses the dielectric-loss factor, dielectric heat-loss factor, dielectric coefficient, or loss tangent. The loss usually increases at low frequencies and as the temperature increases. [37]

2.1.3 Ferroelectric materials

The ferroelectric materials are classified into 4 main types according to their structures. They are the corner sharing oxygen octahedras, compounds containing hydrogen bonded radicals, organic polymers and ceramic polymer composites. The corner sharing octahedra type is a large class of ferroelectric crystals in which it can be separated to perovskite type compounds, tungsten bronze type compounds, bismuth oxide layer structure compounds, and lithium niobate and tantalate. Many piezoelectric (including ferroelectric) ceramics such as barium titanate ($BaTiO_3$), lead titanate ($PbTiO_3$), lead zirconate titanate (PZT), lead lanthanum zirconate titanate (PLZT), lead magnesium niobate (PMN), potassium niobate ($KNbO_3$), have the perovskite type structure. [2]

The structure of the perovskite type is ABO_3. It is a cubic at a high temperature, and below the Curie temperature it becomes non-cubic such as tetragonal and rhombohedral and polar. The interesting materials of the perovskite structure are described as follows:

2.1.3.1 Barium titanate

Barium titanate ($BaTiO_3$) is the first perovskite structure that is found to be ferroelectric ceramic. Its Curie temperature (T_c) is about $130^{\circ}C$. The barium titanate has a paraelectric cubic phase above T_c. It shows the ferroelectric tetragonal phase in the temperature range $130^{\circ}C$ to $0^{\circ}C$ and the spontaneous polarization is along one of the [001] directions in the original cubic structure. The ferroelectric orthorhombic phase occurs between $0^{\circ}C$ and $-90^{\circ}C$ and it is stable with the polarization along one of the [110] directions in the original cubic structure. The phase transition from the orthorhombic to the ferroelectric rhombohedral phase when the temperature is decreased below $-90^{\circ}C$ and the polarization is along one of the [111] directions in the original cubic structure.[2,8]

It is the first piezoelectric transducer ever developed. However, it has shifted away from transducers to high dielectric constant capacitors of the discrete and multilayer (MLC) types in the next time. There are two reasons for this, the first, T_c is low so it is difficult for using in high power transducers. The latter reason is low electromechanical coupling factor in comparison to lead zirconate titanate (0.35 vs 0.65), which limits its operational output. The properties of $BaTiO_3$ must be adjusted with many modifiers for good applications. Sr^{2+} substitutions to the A site have been found to reduce the Curie point linearly towards room temperature, while Ba^{2+} is substituted with Pb^{2+} for increasing the Curie temperature. Moreover, the stable temperature range of the tetragonal phase is increased with Ca^{2+} and the high electric field loss is decreased with Co^{2+}, which does not affect the piezoelectric constant.[1,2]

2.1.3.2 Lead titanate

Lead titanate (PbTiO$_3$) is a ferroelectric material having a structure similar to barium titanate with a high Curie point (490°C).[2] In addition, it is a low dielectrical quality factor and high stability, and also it is a desirable stable piezoelectric material for high-frequency and high-temperature applications. Initially, ceramics of high PbTiO$_3$ content are very porous and fragile because of the strong spontaneous strain occurring at their cubic-tetragonal transition.[34] However, the spontaneous strain developed during cooling can be reduced by modifying the lead titanate with various dopants, such as Ca, Sr, Ba, Sn, and W to obtain a crack free ceramic.[2]

2.1.3.3 Lead zirconate titanate (PZT)

Lead zirconate titanate, Pb(Zr$_x$Ti$_{1-x}$)O$_3$ is a perovskite structure with Ti^{4+} and Zr^{4+} ions occupying the B site at random as shown in Fig. 2.4. It is a binary solid solution of lead zirconate (PbZrO$_3$) and lead titanate (PbTiO$_3$). Fig. 2.5 shows the phase diagram of PZT as a function of composition and temperature.
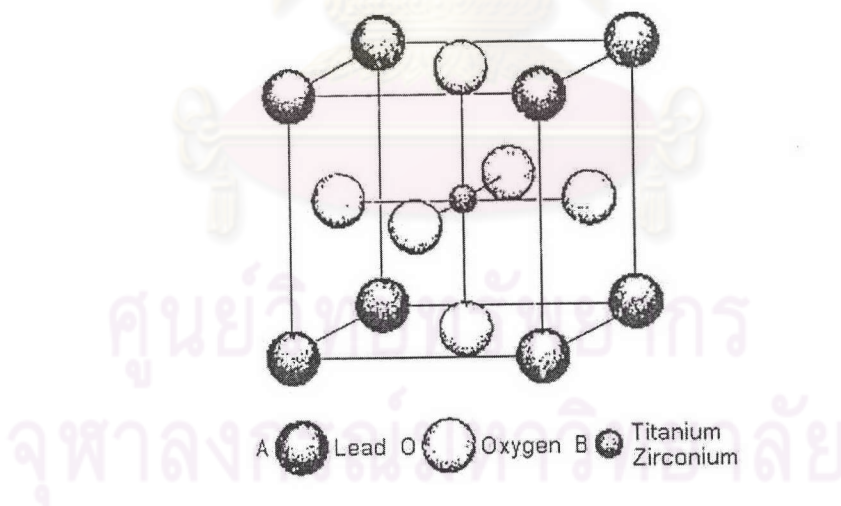

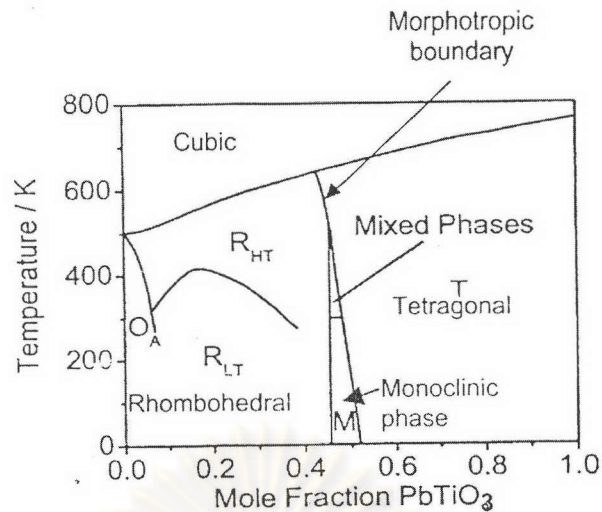Fig. 2.4 The PZT crystal structure above Curie temperature.[19]

Fig. 2.5 The sub-solid phase diagram of PZT ceramics.[8]

The lead zirconate titanate has a cubic phase at high temperature and this phase is a paraelectric. When the temperature is decreased below the Curie temperature (T_c), the cubic phase is transfered into a ferroelectric tetragonal or rhombohedral phase. At the morphotropic phase boundary (MPB); Zirconium/Titanium ratio of 53/47 at room temperature; transition occurs between the rhombohedral zirconium-rich phase and the tetragonal titanium-rich phase. The PZT shows the highest piezoelectric d_{33} constant, dielectric constant, and electromechanical coupling factor at this composition. Furthermore, the poling at the MPB is also easy because the spontaneous polarization within each grain can be switched to one of the 14 possible orientations (eight [111] directions for the rhombohedral phase and six [100] directions for the tetragonal phase). Recently, it has been found that very pure and carefully prepared a PZT ceramic of the morphotropic boundary composition is a monoclinic phase (24 orientations) at room temperature. This may explain the culmination of the dielectric and piezoelectric properties at this composition.[2,8]

2.1.3.4 Relaxor ferroelectrics

The relaxor ferroelectrics are a class of lead based perovskite type compounds with the general formula $Pb(B_1,B_2)O_3$ where B_1 is a lower valency cation (like Mg^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}) and B_2 is a higher valency cation (like Nb^{5+}, Ta^{5+}, W^{5+}). The representative materials of this class are lead magnesium niobate (PMN), lead zinc niobate (PZN), and lead magnesium niobate zirconate (PMNZ).[2,8,35]

The relaxor ferroelectrics like PMN can be distinguished from normal ferroelectrics, such as $BaTiO_3$ and PZT, by the presence of a broad diffused and dispersive phase transition on cooling below the Curie point. They show a very high room temperature dielectric constant and a low temperature dependence of dielectric constant. The diffused phase transitions in relaxor ferroelectrics are due to the compositional heterogeneity seen on a microscopic scale. The relaxors also show a very strong frequency dependence of the dielectric constant. If frequency increases, the Curie temperature will be increased too.[2]

They are thought to consist of weakly interacting mesoscopical ferroelectric regions rather than the usual coherent microscopic ferroelectric domains. This feature leads to many useful properties: a) very high permittivity over a wide temperature range, b) large electrostrictive strains, c) strong piezoelectric activity when the material is under a dc bias field, and d) strong electrooptic activity. They are used in many applications, for example, high electrostrictive actuators, high dielectric constant capacitors.[1,8]

2.1.4 Applications of ferroelectric materials

The ferroelectric materials are widely used in many field applications. Especially, ferroelectric ceramics, they have a number of properties, which make them very useful in a variety of applications. There are (1) high dielectric constants, (2) high piezoelectric constants, (3) relatively low dielectric loss, (4) high electrical resistivity, (5) moisture insensitivity, (6) high electromechanical coupling, (7) medium hardness, (8) fairly high pyroelectric coefficients; and in some special compositions, also (9) high optical transparency and (10) high electrooptic coefficients.[23]

They are used by the direct piezoelectric effect, the converse piezoelectric effect or both effects. Examples of piezoelectric applications include the following:[15,23]

High-voltage generators: gas ignitors, impact fuses, flash bulb, actuators

Ultrasonic generators: ultrasonic cleaners, sonar, atomizers, ultrasonic

welddings, intrusion alarms, pest control devices

Sounders: loudspeakers, tone generators, head sets, buzzers, alarms

Sensors: accelerometers, hydrophones, auto diagnostic devices, flaw detectors

Resonators: surface wave filters, delay lines, piezoelectric transformers

Miscellaneous: relays, pumps, motors, fans, positioners, printers, touch controls

They are also utilised for ferroelectric applications, such as ferroelectric memories, energy conservation devices, security locks.[23] In addition, these materials are used as dielectric materials for capacitor components because of their high dielectric constants.[2] Moreover, they are applied in electrostriction and electrooptic applications, such as optical waveguides and optical memory displays.[1,2]

2.2 Screen printing technique for thick film technology

2.2.1 Introduction

Thin film, thick film, and bulk component are separated by the thickness. The thickness of the thick film is between 1 and 100 μm. If the thickness of the film is equal or lower than 1 μm, it is called the thin film. For the bulk component, the thickness is equal or higher than 100 μm. The thick film technology is developed for many applications, for example, resistor networks, hybrid integrated circuits, hybrid integrated networks, and discrete components, such as resistors, capacitors, and inductors.[8,9]

Fabrication methods are widely used for the thick film, which are a tape casting, sol-gel spin coating, and screen printing. In the tape casting, ceramic/electrode layers are laminated under dry conditions and a binder system in dried tape must have good handling properties, i.e., good elasticity, which unfortunately means a large proportion of organic. All these environmental conditions in this technique increase the risk of delamination problems during lamination and sintering procedure. On the other hand, in the screen printing technique, the formation of multilayer is performed with a wet paste and the amount of organic materials is much lower.[10] A film cracking is the main problem in the sol-gel technique since an internal stress is occurred in the gel during

drying process. A film thickness higher than 10 μm is difficult to derive from this method because of this problem.[16,17] Moreover, the processing time is required to make thick films so this process is impractical for large scale production.[12]

For the case of screen printing technique, it is widely used in the thick film fabrication because it has several advantages over other methods. The equipment to produce the pattern is relatively cheap and simple, the machine is not complex, and the thickness is controllable. It provides a precise and efficient technique for the fabrication of thick films having thickness between 5 and 100 μm and line width as small as 10 μm. Furthermore, it is versatile and reproducible.[11,12] The screen printing consists of a thick film paste, screen, substrate, and squeegee of which the process is shown in Fig. 2.6. The screen frame is held above the substrate, then the paste is applied to the screen, after that the squeegee passes over the screen frame, pressing the paste through the screen onto the substrate.

2.2.2 Principles

2.2.2.1 Screen

A screen is composed of three main parts, such as a frame, a mesh, and a stencil. Metals and aluminium alloys are usually made for screen frames. On the other hand, wood and plastic frames are used for industrial and fine art screen printing, these materials are not sufficiently stable for thick film applications.[11] Materials commonly utilized for the mesh of screen are categorized into three types. They are a nylon, polyester, and stainless steel. The nylon monofilament is strong and resilient but it can absorb water so it is affected by changes in humidity and temperature. The polyester is very much more stable than the nylon. It is good resilient and sufficiently flexible so it can be used with irregular substrates. The polyester is the most common mesh used for an industrial screen printing and can often be used for the thick film printing. The stainless steel mesh is stronger and more stable than the nylon and the polyester but it is low resilient. It is good wear resistance and so can give a longer life. The stainless steel mesh is appropriate for smooth substrates and high resolution thick films on small areas. Moreover, the open area of the mesh has effect on the passage of paste to the

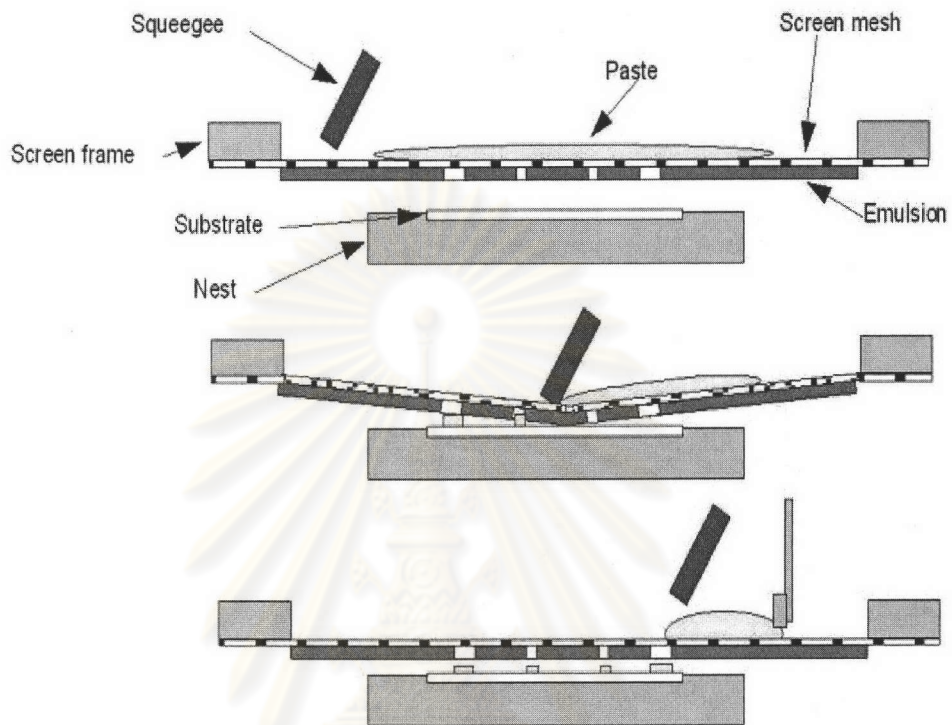substrate. The open area of the mesh depends on a mesh aperture and a thread diameter.[11,13]

Fig. 2.6 The basic screen printing process.[11]

2.2.2.2 Squeegee

The squeegee is commonly made of polyurethane because of its flexibility material and wear resistance. Furthermore, it should not be attacked by constituents of the paste. The squeegee has a wide range of hardness but the hardness normally used for is between 60 and 80 Shore. The common hardness for the general thick film printing is 65 Shore. It has three functions. Firstly, it presses the screen into line contact with the substrate. Secondly, it pushes paste down into the stencil and onto the substrate. Lastly, it cuts the paste level with the top of the screen.[13]

The squeegee dimension should extend beyond the substrate by a minimum of some 10 mm on each side, because a screen tension tends to lift the ends of the squeegee. A screen life is inversely proportional to a squeegee size. A wider squeegee

will reduce screen life since the screen will be over stretched. The squeegee shape is separated into three types such as diamond section, blade or trailing edge section, and knife edge section. The diamond section and the trailing edge section are commonly used. Fig. 2.7 shows all these squeegee shapes including three types.

In classic screen printing, the trailing edge squeegee is brought to use in this field. It can be used with uneven surface of substrates as it is inherently flexible but it is not appropriate with an extremely high viscosity paste. On the other hand, the diamond squeegee can be used with very viscous paste but it limits its ability to conform with uneven substrate surfaces.[11]
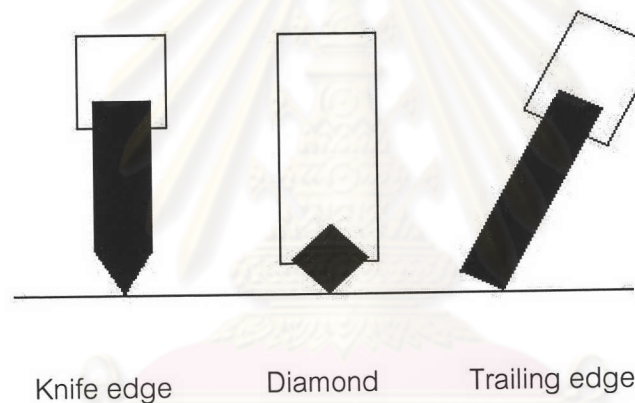

Knife edge   Diamond   Trailing edge

Fig. 2.7 Squeegee shapes.[11]

2.2.2.3 Paste

The paste using in thick film applications is dispersion of an inorganic oxide or a metal powder in an organic fluid vehicle system. The thick film paste has three important parts. Firstly, a functional phase can be metal or semiconducting oxide powders for resistor compositions, metal powders for conductor compositions, or glass and/or ceramic powders for dielectric compositions.[9] In the case of the ceramic powders, there are many kinds for using in dielectric applications, for example, glass, $BaTiO_3$, PZT, and etc. Secondly, a permanent binder is used to adhere the fired film to its substrate and it results in lowering the sintering temperature. It can be subdivided into

two groups, which are glasses and oxides, such as borosilicates and CuO, respectively. However, it may be mixed between oxides and glasses to produce mixed bonded compositions.[4,5,9] Lastly, a vehicle typically contains two components: a volatile solvent, such as terpineol and a nonvolatile resin, such as ethyl cellulose and acrylate. They have different roles in the thick film paste. The solvent reduces viscosity and makes the compositions that can be printable, while the resin (temporary binder) provides flowability of ceramic precursors, the unfired film adherence to the substrate and green strength before firing.[9,26] The vehicle determines the drying rate of the compositions on the screen and the printed film. In addition, dispersing and stabilizing agents may also be added to affect viscosity stability, printability, and shelf life. Moreover, the paste may be mixed with ingredients to control sensitivity of the paste to environment, temperature, drying, and firing.[9,20]

The screenability of thick film paste depends on many factors and rheology is one of them. In practice, the rheology of the paste is strongly influenced by the total loading of the solid materials, by the particle size and particle size distribution of the powders, and by the organic binders. The rheology behavior can be separated into two major groups, a Newtonian viscous fluid and a Hookean elastic solid. Most materials, however, exhibit mechanical behavior, which is intermediate between these two groups. The materials are both viscous and elastic characteristics in evidence and they are called viscoelastic.[10,20,21] Fig. 2.8 shows typical types of rheological behavior.
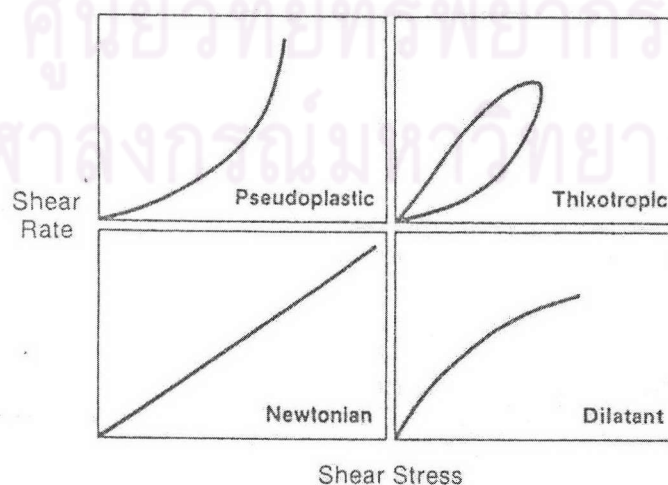

Fig. 2.8 Responses of fluid to shear.[9]

A Newtonian behavior in Fig. 2.8 means shear rate is linear with applied stress. The viscosity of this behavior is independent with shear rate. A theoritically ideal paste would show this behavior. However, it may only be expected from low-viscosity liquid systems but common thick film pastes very seldom act this behavior.

A non-Newtonian behavior has two major groups, such as a steady state phenomena, for example, dilatant and pseudoplastic, and a time-dependent phenomena, for example, thixotropic. The dilatant or shear thickening is characterized by an increase in apparent viscosity with increasing rate of deformation. This behavior impedes printing. On the other hand, the pseudoplastic or shear thinning is characterized by a gradual decrease in apparent viscosity with increasing rate of shear. The thixotropic is the one type of the time-dependent phenomena. It is analogous with shear thinning behavior as viscosity of them decrease when the shear rate increase and recovery to high viscosity on cessation of shear. The thixotropic behavior, however, shows hysteresis loop; the viscosity at a given shear rate is usually higher with increasing shear rate than when the shear rate is decreasing. A thixotropic hysteresis loop is illustrated in Fig. 2.8. Most pastes of thick films exhibit the pseudoplastic or thixotropic rheology with viscosity as an inverse function of shear rate.[9,20,21]

A firing process controls properties of thick films for using in many applications. In this process, the vehicle should be completely burnt out because it may affect the properties of thick films. A temperature profile is important for firing of the thick films. Fig.2.9 shows thermal events in the thick film firing process. From Fig. 2.9, First, the volatile portion of the vehicle evaporates. After that, the nonvolatile phase is burnt at temperatures between 200°C and 400°C. The permanent binder begins to flow or react with the substrate when the temperature is increased. The functional phase is reacted with the permanent binder and sintered at the elevated temperature.
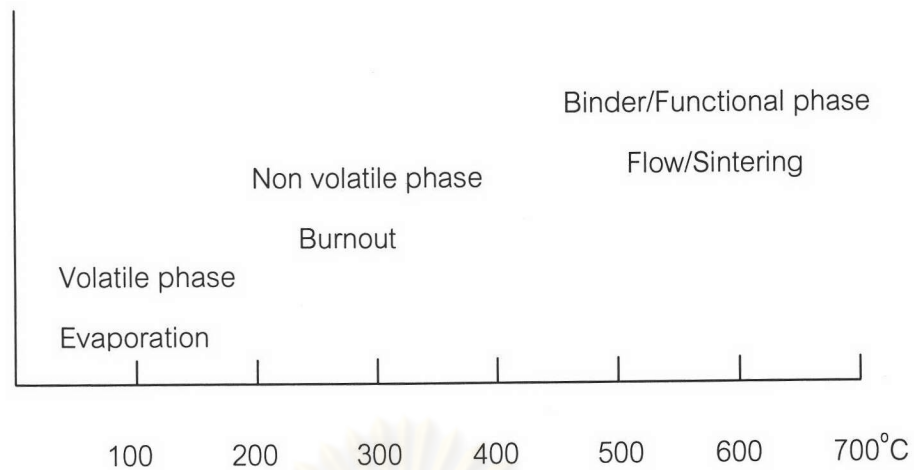
Fig. 2.9 Thermal events in the thick-film firing process.[9]

2.2.2.4 Substrate

In thick film processing, the surface chemistry and surface condition of the substrate is more important than the bulk property of it. The surface may be reacted with the compositions of thick film during firing and undesired phases occur. These phases affect many properties of thick films, for example, electrical and mechanical properties. Fig. 2.10 shows the concentration profiles of the dissolution of an alumina substrate into typical thick film resistor and diffusion of PbO into the substrate. The Pb diffuses to a depth of approximately 4 microns.

The standard substrate for thick film industry has been 96% alumina (Al_2O_3). This substrate has excellent electrical characteristics, high thermal conductivity, good dimensional stability, excellent mechanical strength, and is a chemically inert material.[9] The alumina substrate, however, is very brittle and it is difficult to create complicated mechanical structures. This problem can be solved by using a silicon wafer substrate. It is possible to use isotropic and anisotropic etchants in order to create cavities, beams, cantilevers and other mechanical structures. However, it may react with the compositions of the thick film to decrease mechanical and electrical properties.[26]

In this study, a stainless steel is chosen for using as a substrate. The stainless steel is iron–based alloys that contains a minimum of approximately 11% Cr, the amount is needed to prevent the formation of rust in unpolluted atmospheres.[6] It can be divided to five main groups, such as ferritic, austenitic, martensitic, duplex, and precipitation

hardening. The ferritic stainless steel, such as 430 type, which is chromium–iron alloys 17-27% chromium and low carbon content is used in this research.[6,18] This stainless steel type is less costly than 304, 316, superaustenitics, or duplex grades because of its lower alloy contents.[6]

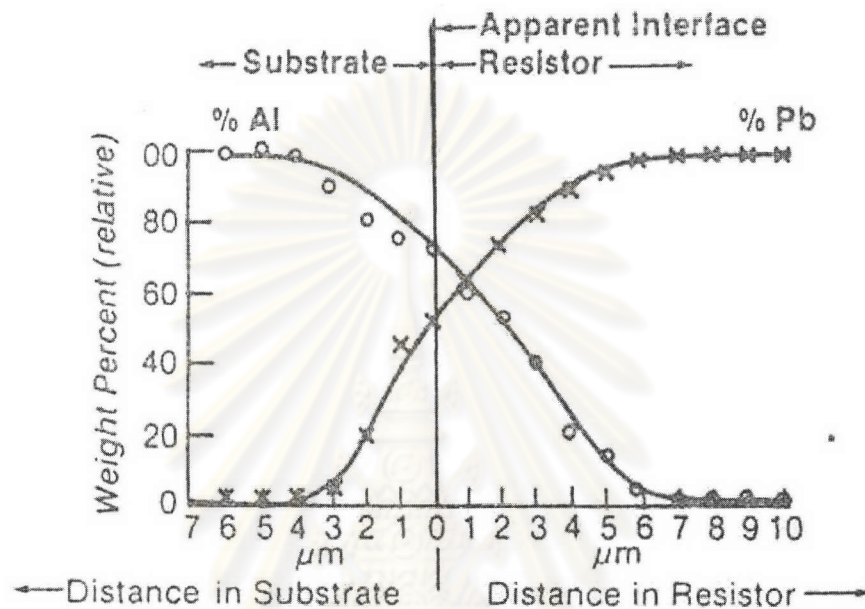

Fig. 2.10 Concentration profiles showing dissolution of Al_2O_3 in resistor and diffusion of PbO in substrate.[9]

2.2.3 Screen printing parameter

2.2.3.1 Snap off

The snap off is a distance between a bottom of the screen and a top of the surface being printed.[9] In a single printed layer, the surface being printed is same as the surface of the substrate. In complex multilayers, they are different because the surface being printed is not the substrate but it is the first printed layer or more, and therefore, the snap off distance must be changed for each layer. The ratio of the screen diameter to snap off distance should be 200:1.[9] The snap off distances i shown in Fig. 2.11. The snap off distance has effect on the print thickness, the print thickness increased when the snap off distance increased.[11]
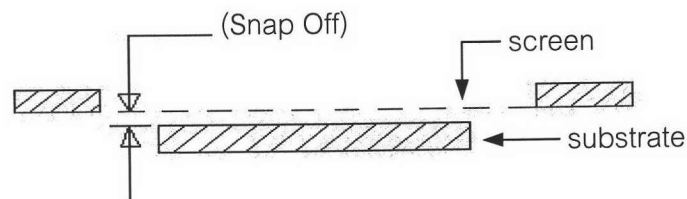
Screen Size	Snap Off (Normal)		For Equal Force
5×5	.025 →	.030	.025
5×7	.025 →	.030	.025
8×10	.025 →	.040	.040
12×12	.035 →	.045	.060

Note : 200:1 Screen Diameter to Snap Off.

Fig. 2.11 Typical snap off distance.[9]

2.2.3.2 Attack angle

The attack angle is an angle between the leading edge of the squeegee and the surface being printed.[9] Fig. 2.12 shows three different attack angles in common use for printing thick film compositions. The thickness of the printed film will be increased when the attack angle decreased. The most attack angle widely uses is 45°.

2.2.3.3 Squeegee pressure

The screen mesh is pressed down towards the substrate by the squeegee pressure and so it affects the thickness of the printed film. If the squeegee pressure is increased, the thickness of it will be decreased. A quantity of the squeegee pressure should be appropriate because too little it will occur an uneven printed film, while too much will cause spreading of the paste.[10,11]
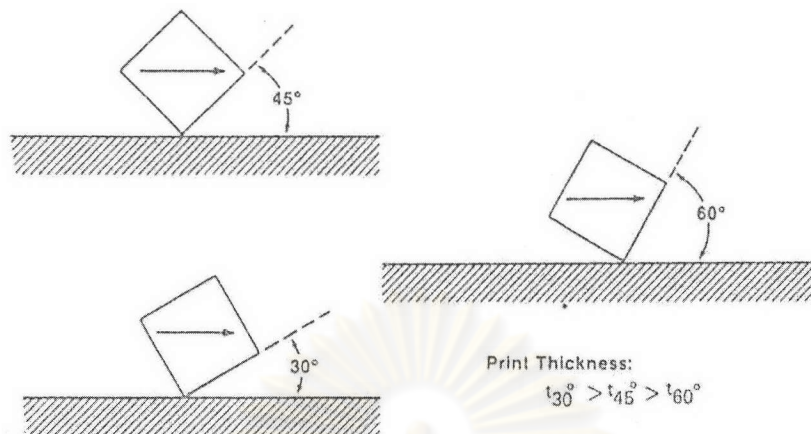
Print Thickness:
$t_{30°} > t_{45°} > t_{60°}$

Fig. 2.12 Three common attack angles (control transfer mechanism).[9]

2.2.3.4 Squeegee speed

The squeegee speed is the speed with which the squeegee travels across the screen. It is another factor, which controls the thickness of the printed film. At high speed, the squeegee will tend to float over the surface being printed, thus increasing the thickness of the printed film. In a general principle, high viscosity pastes require the slowest squeegee speeds.[11]

2.2.3.5 Squeegee hardness

A unit of the squeegee hardness is Shore, for example, 80 Shore is harder than 70 Shore. The most common squeegee hardness used for thick film printing is about 65 Shore which optimises lack of distortion with flexibility. The printed thickness is depended on the squeegee hardness because a hard squeegee deforms less under pressure than a soft one. The attack angle of the hard squeegee is greater than a soft one therefore the printed thickness is decreased.[11]

2.2.3.6 Downstop

The downstop is a mechanical limit of squeegee onto which travels the substrate. It prevents the screen from damage. If the downstop is raised, the squeegee is also raised, thus increasing the printed thickness.[11]

2.3 The previous researches

Thiele, E.S. and Setter, N.[28] worked on the effect of eight commercial dispersants on viscosity of PZT/Terpineol suspensions. They used a rheometer to evaluate the efficiency of the various dispersants. Suspension viscosities were measured at several individual shear rates between 10 and 150 s^{-1}. From this experiment, the dispersant could be divided into two main groups; an ineffective dispersant and an effective dispersant. The ineffective dispersant showed shear-thinning behavior that the viscosity of it decreased when a shear rate was increased. On the other hand, an effective dispersant exhibited Newtonian behavior that the viscosity was not dependent on the shear rate. Examples of the effective dispersants were menhaden fish oil, polyester/polyamine copolymer (Hypermer KD-1), fatty acid polymer derivative (Perfad 9100), and phosphate ester (PS-21A) and the most advantageous dispersant was PS-21A. They also studied how to optimize the quantity of the PS-21A for PZT inks and the minimum viscosity point was 0.1 wt%.

Furthermore, they found the viscosity of the PZT ink containing PS-21A was at least 50% lower than the viscosity of the ink without PS-21A at the shear rate of 10 s^{-1}. At the higher shear rate of 100 s^{-1}, the viscosity of the PZT ink containing PS-21A was at least 30% lower. The PZT powder could be increased in the PZT ink because of these phenomena. This higher concentration was advantageous because it decreased the amount of the solvent evaporation during film drying and the fired films were thicker. The addition of the dispersant improved the microstructural homogeneity of screen-printed thick-film layers and this dispersant did not affect dielectric and piezoelectric properties of the PZT powder.

Thiele et al.[27] developed suitable electrodes and PZT sintering aids that yielded attractive piezoelectric properties to device, while minimizing reactions between the silicon, the bottom electrode, and the PZT thick film. The PZT powder (soft PZT grade, BM500) was mixed with a sintering aid (B_2O_3-Bi_2O_3-CdO or borosilicate glass) in an attritor with ethanol solvent for 2-4 hours. The PZT ink was prepared on a laboratory-scale three-roll mill using terpineol as a solvent, ethyl cellulose as a binder, and a phosphate ester as a dispersant. After that, it was screen-printed onto the silicon substrate with the electrode inks (platinum, gold, Au-Pt-Pd alloy, Ag-Pd alloy, or bilayer

Pt/gold) on the top surface of them and then they were dried at 120°C for 30 min. In the next step, they were fired at various temperature-time profiles.

From this study, they found the dielectric constant of the PZT film with Au-Pt-Pd alloy or Ag-Pd alloy electrode was 60 (film thickness 10 μm). This low value was believed due to the presence of glass additives in both inks, which the glass additives reacted with the PZT film and then it was high density after firing at 850°C. While the dielectric constant of the PZT films with gold electrode exhibited nearly 120. The dielectric constant is higher than aforementioned value because the gold conductor contained no glass, which was likewise consistent with the porosity in the PZT films after firing to 850°C.

However, they continuously tested a bilayer bottom electrode. A layer of pure platinum ink was screen-printed onto the silicon substrates followed by a layer of gold ink and the two inks were cofired on the substrates for 30 mins at 850°C –900°C. After that, the PZT inks were screen- printed on them and then firing. The dielectric constant was increased. It was 970, while the PZT film with gold bottom electrode was 440, thickness of the PZT films were same as 20-40 μm after firing at 900°C for 1 hour. In the case of sintering aids, the B_2O_3-Bi_2O_3-CdO sintering aid was more effective than borosilicate glass because the dielectric constant of the PZT film with B_2O_3-Bi_2O_3-CdO sintering aid was higher. They concluded that the PZT film prepared with B_2O_3-Bi_2O_3-CdO sintering aid, screen-printed onto a Au/Pt bilayer bottom electrode, and sintered at 900°C for 1 hour was the best result. The dielectric, piezoelectric, and ferroelectric properties of this PZT thick film closely approached the bulk PZT.

Wangchokphadung et al.[13] studied the fabrication of PZT thick film on a stainless steel substrate by screen printing technique. The PZT materials were prepared from two routes; a conventional mixed oxide and a sol-gel technique. The conventional mixed oxides, PbO, ZrO_2, and TiO_2 were milled in a ball mill with an acetone solvent for 48 hours. After that, they were dried at 100°C and fired at 890°C for 2 hours. The particle size of the PZT powder from this technique was reduced by an attrition mill. For sol-gel method, the PZT solution was prepared from lead (II) acetone trihydrate, zirconium (IV) propoxide, and titanium (IV) isopropoxide with 2-methoxyethanol solvent. In this research, PbO-B_2O_3-Bi_2O_3 frit was used to reduce the sintering temperature.

The PZT inks were prepared in various compositions. The PZT ink formula was composed of PZT solvent, of which the viscosity changed after one week. This ink could not be printed. In addition, the small PZT powder from the sol-gel technique was believed to cause aggromerates. They also discovered that the frit connected the PZT particles after firing. The best PZT ink consisted of the PZT powder from mixed oxide, frit, terpineol, and ethyl cellulose. This PZT film showed microstructural homogeneity after firing at 750°C for 30 min but the porosity remained. The PZT film on stainless steel substrates showed the dielectric constant and the dissipation factor were 110 and 0.25, respectively at 1 kHz frequency. The dielectric constant was low that might come from the oxide layers on the surface of the stainless steel substrate or lead chromate phase in the PZT film. When the substrate changed from the stainless steel to Pt coated silicon, the dielectric constant and dissipation factor were 460 and 0.05, respectively.

Morissette, S.L. and Lewis, J.A.[29] researched about influence of paste rheology on print morphology and component properties. The PNZT $((PbZr_{0.52}Ti_{0.48})_xNb_{1-x}O_3)$ powder was derived via a coprecipitation method, which it was served as the ceramic phase in this study (as-received powder). Its particle size was reduced by attrition mill and it was called an attrition-milled powder. α-Terpineol (boiling point about 220°C) served as the low-volatile solvent. Ethyl cellulose with molecular weight of 10500 by estimated was used as the binder phase. Four types of dispersants were examined; a polyenoic acid (Menhaden fish oil,MFO), a phosphate ester (Emphos-21A), a fatty acid (Oleic acid), and a fatty acid ester (Hypermer PS-3).

In the initial experiment, they examined the effectiveness of dispersants, maximum packing fraction, and the effect of binder content on the rheological behavior of the ethyl cellulose/terpineol vehicle system. The apparent viscosity of PNZT suspension consisted of PNZT powder, α-Terpineol, and dispersant, was measured. The PNZT suspension with Hypermer PS-3 or MFO dispersant exhibited the lowest apparent viscosity and degree of shear thinning, suggesting that these dispersants provided the most effective stabilization of the PNZT particles. However, Hypermer PS-3 was difficult to dissolve in concentrated suspensions. The menhaden fish oil was chosen for additional experiments. For the rheological behavior of the ethyl cellulose/terpineol vehicle system, it showed Newtonian behavior. Furthermore, the suspensions prepared

from the as-received powder exhibited significantly higher relative viscosity at a given solid volume fraction when compared with the dispersant-coated attrition-milled powder because of the agglomerates in the as-received powder.

The PNZT thick films were prepared via computer-aid direct-deposition of PNZT pastes onto dense alumina or Teflon substrates using a commercial micropen system and they were fired at varying maximum temperatures. Dielectric constants ranged from 1265 to 1570 depending on a frequency and a sintering temperature. The highest value of 1570 was measured at 1 kHz frequency for samples sintered at 1050°C for 5 hours. These values increased when the sintering temperatures were increased because of higher film density. The dissipation factors showed less than 4.5% were measured at all frequencies.