CHAPTER 2

LITERATURE REVIEW

This chapter contains details on the general background of electroceramic material selected for this study: Lead Zirconate Titanate (PZT). The relevant literatures on PZT, sol-gel process and fabrication of ferroelectric thin films are given as well. This chapter also introduces the concepts of identification and characteristic of PZT thin films.

2.1 Lead zirconate titanate

A solid solution system $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) has now been the most widely exploited of all piezoelectric ceramics because it possesses higher electromechanical coupling coefficients than other popular ferroelectrics and higher Curie temperature (T_c) values which enable higher operation or processing temperatures during fabrication of devices. Moreover, PZT can be easily poled, requires low sintering temperature and possesses a wide range of dielectric constants. It forms solid-solution compositions with many different constituents, thereby achieving a wide range of properties [38]. Since its discovery as a ferroelectric material in 1940s, PZT has been considered as the best ferroelectric and piezoelectric material. PZT has a perovskite structure (also regarded as a cubic close-packed arrangement), and the structure can be considered as a face-centered-cubic (FCC) derivative structure in which the larger A cation and oxygen together form an FCC lattice. The smaller B cation occupies the octahedral site in this FCC array and has only oxygen as its nearest neighbor. As shown in Fig. 2.1, the A-site cation is Pb^{2+} occupying the corners of a cube while the Ti^{4+} and Zr^{4+} ions occupying the B-site in the center of the body.

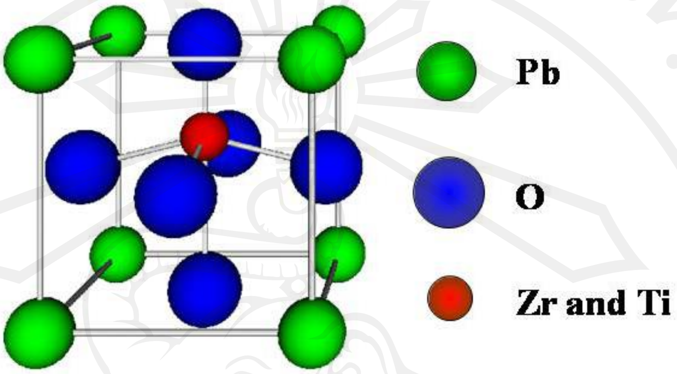

Figure 2.1 Perovskite-type structure of PZT

PZT is a binary solid solution of an anti-ferroelectric $PbZrO_3$ (orthorhombic structure) and a ferroelectric $PbTiO_3$ (tetragonal perovskite structure). The phase diagram of PZT is shown in Fig. 2.2. The boundary between the tetragonal and rhombohedral form which is nearly independent of temperature is called morphotropic phase boundary (MPB). The compositions similar to MPB have been extensively exploited in a commercial field [39, 40]. The early investigation of piezoelectric properties in this ceramic system showed the electromechanical coupling factor and dielectric constant to be the highest near MPB (Fig. 2.3). The poling of PZT ceramic is also achieved easily for this composition since spontaneous polarization within each grain can be switched to one of the 14 possible orientations: 8 [111] directions for the rhombohedral phase and 6 [100] directions for the tetragonal phase [40]. Excellent piezoelectric and electrostrictive properties make PZT a promising material for ferroelectric memory, non-volatile random access memory, electrostrictive actuator and transducer applications [38].

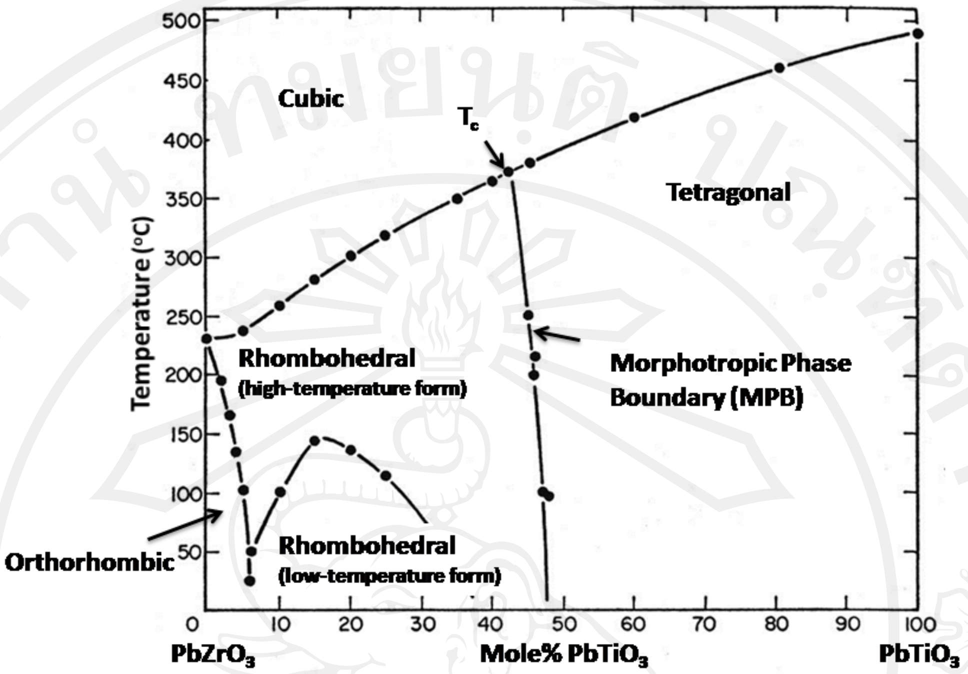

Figure 2.2 Phase diagram of the $PbTiO_3$-$PbZrO_3$ solid solution [40]

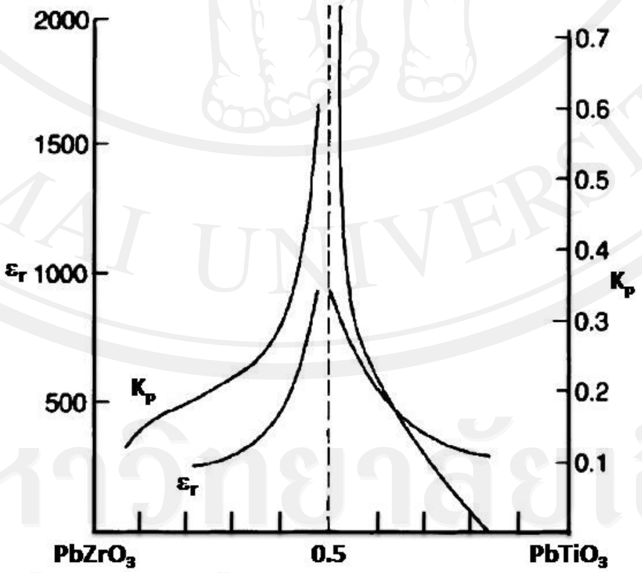

Figure 2.3 Composition dependence of a dielectric constant and an electromechanical coupling factor in PZT ceramic [40].

PZT ceramics are generally used in the form of monoliths connected to an external electronic circuit. Many devices can, therefore, be significantly reduced in size and weight if the same electrical properties are produced in the form of thin films [1].

2.2 Doping effect on PZT ferroelectricity

In general, the term “doping” of piezoelectric ceramics implies that some ions, whose chemical valences are different from those of the original ions in the lattice or some compounds with a chemical formula $A^{+}B^{5+}O_3^{2-}$ or $A^{+}B^{3+}O_3^{2-}$, are added to the PZT piezoelectric ceramics. The small amount of dopants can drastically change dielectric, electro-mechanical and electrooptic properties of ceramics [41].

Moderate concentrations of higher-valent A-site or B-site substitutions are known to result in enhanced weak-field dielectric and piezoelectric properties, reduced coercive fields, and higher electromechanical coupling coefficients at the expense of significantly enhanced weak-field dielectric loss factors in a ferroelectric state [40]. The materials with these properties moderately modified by the higher valent substitutions on A-site or B-site are generally called “soft” PZT. In contrast, the materials whose properties are moderately modified by the lower valent substitutions on A-site or B-site are called “hard” PZT. Moderate concentrations of lower-valent substitutions on A-site or B-site are known to result in reduced weak-field dielectric and piezoelectric constants, lower weak-field dielectric losses, and higher coercive fields [40].

Table 2.1 Common aliovalent substitutions and effects of PZT ceramics relative to undoped PZT ceramics [39].

Classification	**Position for doping**	**Dopants**	**Effects**
“Soft” PZT	A-site donors	La^{3+}, Bi^{3+}, Nd^{3+}	Reduced oxygen vacancies Increased volume resistivity Increased domain wall mobility High dielectric, piezoelectric constant High dielectric loss Low mechanical quality factor Easy poling, low coercive field
	B-site donors	Nb^{5+}, Sb^{5+}, W^{6+}	
“Hard” PZT	A-site acceptors	K^{+}, Rb^{+},	Increased oxygen vacancies Decreased volume resistivity Decreased domain wall mobility Low dielectric, piezoelectric constants Low dielectric loss High coercive field Hard poling, and depoling
	B-site acceptors	Co^{3+}, Fe^{3+}, Sc^{3+}, Ga^{3+}, Cr^{3+}, Mn^{3+}, Mg^{2+}, Cu^{2+} Al^{3+}	

The complex variations in the properties of PZT resulting from different doping are presented in the following sections. Common aliovalent substitutions and effects of PZT ceramics relative to undoped PZT ceramics are summarized in Table 2.1.

2.2.1 Soft doping

The softening effect of PZT soft doping is attributed to a creation of Pb vacancies in the perovskite lattice when the soft doping ions enter the lattice structure. Since Pb^{2+} ions occupy the A-sites of the perovskite lattice, soft doping ions create the A vacancies. In general, ions with larger ionic radii, such as La^{3+}, Nd^{3+}, Sb^{3+}, Bi^{3+}, Th^{4+}, occupy the A sites to replace Pb^{2+} ions. When two A sites are occupied by two cations with a valence of +3, a Pb vacancy is created in the lattice to maintain electroneutrality. Likewise, when ions with larger ionic radii, such as Nb^{5+}(0.69 Ǻ), Ta^{5+}(0.68 Ǻ), Sb^{5+}(0.63 Ǻ), W^{6+}(0.65 Ǻ), etc., enter into the perovskite lattice, they occupy the B sites to replace Zr^{4+}(0.79 Ǻ) or Ti^{4+}(0.68 Ǻ) ions. Since the doping ions have a higher valence than +4, extra positive charges enter the lattice, and Pb vacancies have to be created to ensure electroneutrality. In donor doping, for example, Nb5+ introduces Pb vacancy, which is represented as V_{Pb} (equation 2.1).

$$Nb_x + Pb(Zr_yTi_{1-y})O_3 \rightarrow \left(Pb_{1-\frac{x}{2}}V_{Pb\,x/2}\right)(Zr_yTi_{1-y-x}Nb_x)O_3 \qquad \textbf{(2.1)}$$

Since the Pb ion cannot easily hop to an adjacent A-site vacancy due to the surrounding oxygen as illustrated in Fig. 2.4. When, in a lattice with Pb vacancies, the transfer of atoms is easier than in a perfect lattice; thus, domain motion can occurred by a smaller electric field (or a mechanical stress). Therefore, the coercive field of ferroelectric ceramics is reduced.

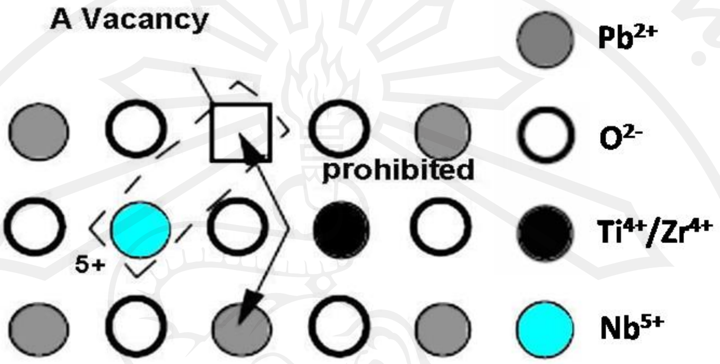

Figure 2.4 Crystal deficiencies in PZT for donor dopant [41].

The mechanical quality factor (Q_m) decreases with increasing internal friction (mechanical loss and electrical loss) because more energy is spent on the domain motion and ionic dynamic processes. Since the domain motion is easier in PZT ceramics with Pb vacancies, the release of internal strain (or stress) takes place more easily. Therefore, after poling, the stress release process in soft-doped PZT is faster than that in an undoped PZT. This enables it to establish a higher stability for physical properties of soft doping PZT within a shorter period of time after poling.

The soft-doped is similar to the donor impurity in semiconductors. When the concentration of donor impurities is close to that of the acceptor originated from Pb vacancies, most of the holes from the acceptor level are compensated by electrons from the donor level. As a result, the bulk resistivity (ρ_v) of soft-doped PZT increases [42]. Consequently, it becomes easier to establish a high electric field in soft doped

PZT because of its high ρ_v value, and domain motion is also easier owing to the Pb vacancies. The combined effect of these two factors, which causes more than adequate realignment of domains, directly results in higher piezoelectric activities in soft PZT in comparison with those in undoped PZT.

Moreover, some donor doping such as W^{6+} in PZT ceramics were reported to increase the polarization switching but reduce the coercive field. Compensation of W^{6+} occurs through the reduction of oxygen vacancies in PZT system [31]. Oxygen vacancies are defects which segregate and pinch the domain walls. This reduces domain movement, resulting in a degradation of ferroelectric switching ability.

2.2.2 Hard doping

Hard doping ions in PZT include: K^+ and Na^+, which occupy the A sites; and Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Mn^{2+}, Mn^{3+}, Ni^{2+}, Mg^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, $Cr^{3+}$and Sc^{3+}, which occupy the B sites in the perovskite structure [43]. Physical mechanisms of hard doping are complex because different hard doping ions affect different properties. In a PZT with Fe^{3+} doping, a dielectric loss (or tan δ) value is usually reduced. This is especially true of the dielectric loss in a strong external field. Therefore, Fe^{3+} ions are an effective hard doping ion for PZT and used in high-power transducers [43].

A hard doping ion is considered as an acceptor since it causes oxygen vacancies in the perovskite lattice. Both A sites and B sites may be occupied by a lower chemical valence ion, one of which is occupied depending on the ionic radius of the doping ion. For example, Pb^{2+} ions may be replaced by K^+ ions, and Zr^{4+} (or Ti^{4+}) ions by Fe^{3+}, Sc^{3+} or Mg^{2+}.

When hard doping ions with a lower positive valence replace metal ions with a higher positive valence, oxygen vacancies are created in the lattice to balance electroneutrality. For example, as the crystallographic deficient occurs due to impurity doping in a perovskite crystal, acceptor ions, such as Fe^{3+} introduce oxygen deficiencies ($V_{Ö}$) to the PZT lattice as expressed in equation (2.2).

$$Fe_x + Pb(Zr_yTi_{1-y})O_3 \rightarrow Pb(Zr_yTi_{1-y-x}Fe_x)O_{3-x/2}V_{Öx/2} \qquad \textbf{(2.2)}$$

This acceptor doping causes deficiency-related dipoles. These dipoles are generated by a Fe^{3+} ion (effectively negative charge) and an oxygen vacancy site (effectively positive charge). The deficiencies are produced at a high temperature (> 1000°C) during sintering; however, oxygen ions are still movable even below a Curie temperature (e.g. room temperature) because the oxygen and the vacancy are adjacent (only 2.8 Å) and can easily hop as illustrated in Fig. 2.5.

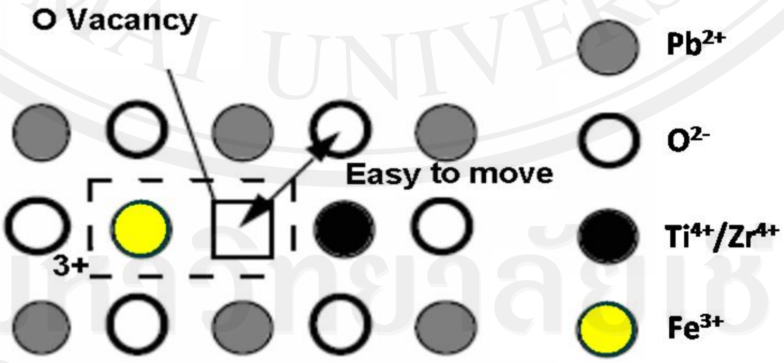

Figure 2.5 Crystal deficiencies in PZT for acceptor dopants [41].

Hard doping ions also inhibit grain growth due to their low solubility in the lattice of solid solution. As a result, a portion of doping oxides precipitate out of normal grains and stay at grain boundaries, which subsequently resist grain growth. Another effect of these precipitates is to accumulate at grain boundaries as bonds, which binds the adjacent grains and thereby enhance elastic stiffness constant as well as mechanical strength.

On the contrary, acceptor-type ions with a small valence +1 to +3 suppress strain and increase hysteresis and coercive field. Although acceptor-type ions must be avoided in designing actuator ceramics used for positioning applications, acceptor doping is imperative to make “hard” piezoceramics which are particularly suitable for ultrasonic motor applications. These dopant effects can be attributed to “domain pinning effect”. An oxygen vacancy is a defect in structure and also is the main cause of domain pinning effect. Defect distribution and mobility have important influences on polarization behavior. However, mobile defects can assemble into extended structures. Such defect structures could be dipolar and interact strongly with domain walls, resulting in polarization pinning. Further evidence is necessary to better identify the role of oxygen vacancies and to support the assumption of substituent-oxygen vacancy complexes as pinning sites [44].

2.3 PZT thin films

Polycrystalline PZT is of major significance in microtechnology, particularly in the field of sensors and actuators because of their superior piezoelectric and pyroelectric properties and high dielectric constants [38]. A further advantage of this material is the low process temperature which is compatible with Si technology [45].

New devices that incorporate these materials include ultrasonic motors, sensors, filters, memory devices and switches. New applications have been emerging, and research efforts have been made to address the manufacturing technology required to incorporate PZT with associated structural components and electronic circuitry at the wafer scale.

The developed thin film compositions have greatly reduced processing temperatures (600-700°C) in comparison with standard bulk ceramic sintering temperatures (1100-1400°C), which has led to commercialization in the form of ferroelectric memories and electronic components by the major electronics corporations. A single layer is about 0.1 µm, and films are built up to the required thickness by depositing several layers. Some studies also succeeded to increase the film thickness by making composite films [46].

The piezoelectric properties of films are most likely smaller than those of corresponding bulk ceramics because of substrate clamping which reduces the amount of strain [47, 48]. The film is a part of the composite structure consisting of piezoelectric film and silicon substrate. The film is clamped in the film plane but free to move in the out-of-plane direction. Consequently, the clamping effect is thickness dependent, and the piezoelectric coefficient, such as d_{33}, increases with increasing thickness over a range of film thickness [49-52]. Piezoelectric coefficients are optimized when the polarization axis, namely *c*-axis or (001), is perpendicular to the film surface [53]. A side from mechanical clamping due to the inert substrate, there are other factors influencing the piezoelectric response of ferroelectric thin films, including orientation [54-56], grain size [57], level of polarization and breakdown field strength [58, 59]. The influence of defects on the domain-wall contributions to the piezoelectric effect in thin films has been largely unknown yet. Thus, it is presently not clear whether, for example, the effect of acceptor and donor dopants on PZT thin film properties leads to the same effects as in bulk materials.

Ferroelectric properties have been present in the area of MEMS application for over 20 years. Numerous works on ferroelectric materials have pointed out that many factors might influence ferroelectric properties (e.g., structure, chemical composition, orientation, defect density, domain structure, substrate type and film thickness). It appears that the optimized growth of ferroelectric epitaxial films can be a viable approach to improve the ferroelectric properties, particularly for the layered perovskites. The defects related to polycrystalline structures cause a degradation of ferroelectric properties like piezoelectric coefficients, remanent polarization and charge retention, which may bring about time dependent fatigue problems. Substitutions of elements allow adjustment of the film properties to the device function. Additionally, film orientation can be controlled the appropriate choice of substrate which is essential due to the anisotropy of the ferroelectricity [60-66]. In fact, for ferroelectric films, the choice of substrate is of primary significance for the growth of high-quality heteroepitaxial films. It is clear that lattice mismatch between film and substrate affects film properties like crystallinity, defect density, microstructure and domain structure [67]. Although the growth of quality PZT thin films requires some more efforts. In film processing, wet chemical methods continue to be the main stream for many applications. Nevertheless, there are many techniques for preparing films, each having its own advantage.

2.4 Fabrication of ferroelectric thin films

The act of applying a thin film to a surface is called thin film deposition. Most deposition techniques regulate layer thickness within a few tens of nanometers. A wide variety of fabrication techniques have been used to manufacture ferroelectric thin films. Thin film synthesis techniques used in laboratory are based on physical or chemical deposition of thin films.

2.4.1 Physical deposition

In physical deposition, solid material is converted to a vapor through heating (evaporation) or energetic ion bombardment. The material in the form of vapor is eventually condensed on the substrate surface as a thin film. Physical techniques use mechanical, electromechanical or thermodynamic means to produce a thin film. An everyday example is the formation of frost. However, commercial physical deposition systems tend to require a low-pressure vapor environment for proper functions. Most can be classified as physical vapor deposition (PVD). The examples of physical deposition are included in the following sections.

2.4.1.1 Evaporation

Evaporation is a common deposition method. The source material is evaporated in a vacuum as shown in Fig. 2.6. The vacuum allows vapor particles to travel directly to the target object (substrate), where they are condensed back to a solid state. A thermal evaporator uses an electric resistance heater to melt the material and raise its vapor pressure to a useful range. This takes place in a high vacuum because evaporated particles can travel directly to the deposition target without colliding with the background gas. The high vacuum also allows the vapor to reach the substrate without reacting with or scattering against other gas-phase atoms in the chamber and reduces the incorporation of impurities from the residual gas in the chamber. Needless to say, only the materials with a much higher vapor pressure than the heating element can be deposited without contaminating the film [68].

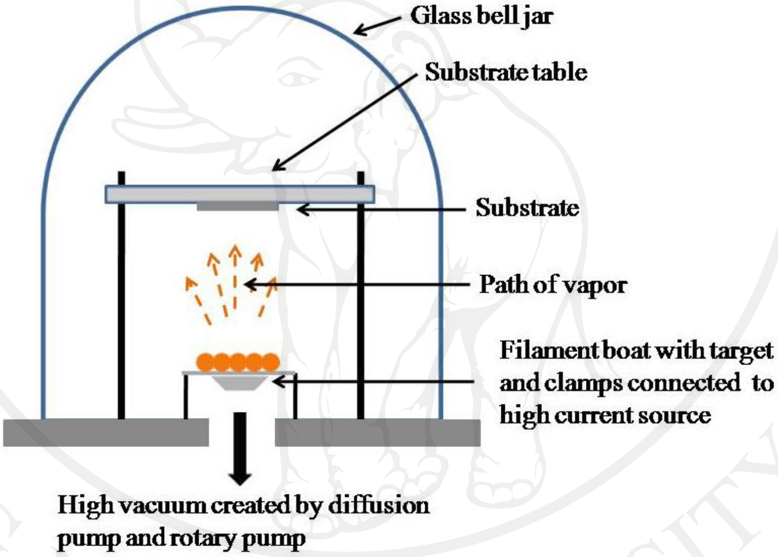

Figure 2.6 Schematic diagram of a resistive thermal evaporation system [68]

2.4.1.2 Sputtering

Sputter deposition is one of the physical vapor deposition (PVD) methods. This involves ejecting material from a "target" onto a "substrate" such as a silicon wafer. When an energetic particle strikes a surface (the target), a plume of material is released. Sputtering relies on plasma (usually in a noble gas such as argon) to knock the material from the target. Argon gas is fed into an evacuated chamber, and the plasma is stuck. The plasma accelerates Ar^+ ions across its sheath potential to strike the target. The incident ions set off collision cascades in the target. If the cascade recoils and reaches the target surface with the energy greater than the surface binding energy, atoms are ejected as depicted in Fig. 2.7. Physical sputtering is driven by momentum exchange between the ions and atoms in the material due to collisions [69].

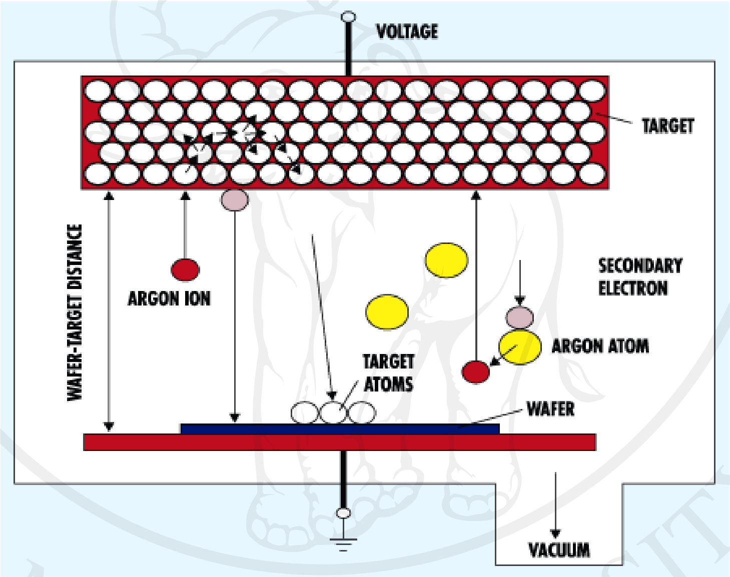

Figure 2.7 Sputter deposition process with argon gas [71]

For efficient momentum transfer, the atomic weight of the sputtering gas should be equivalent to that of the target. Thus, neon is preferable for sputtering light elements while krypton or xenon are used for heavy elements. Furthermore, the target can be kept at a relatively low temperature, making this process the most flexible deposition techniques. This effect is known as 'sputtering' and is used to produce films as thin as just a few millionths of a millimeter. Sputtering is especially useful for compounds or mixture, where different components evaporate at different rates [70].

2.4.1.3 Pulsed laser deposition

Pulsed laser deposition (PLD) is a thin film deposition technique in which a high power pulse laser beam is focused onto the surface of the target inside a vacuum chamber. At sufficiently high energy density and short pulse duration, all elements in the target surface are rapidly raised to their evaporation temperature.

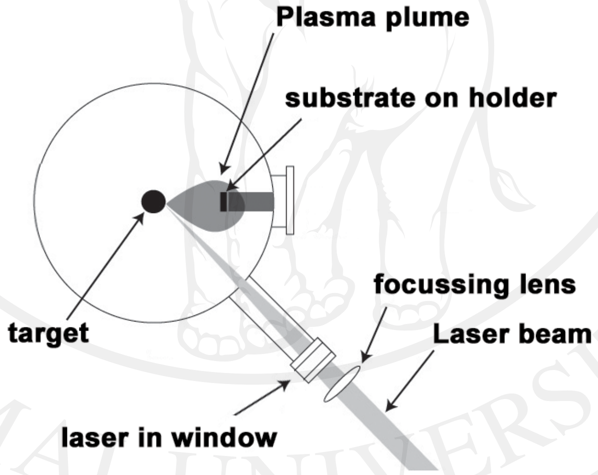

Figure 2.8 Configuration of a PLD deposition chamber [73]

The material is vaporized from the target (in a plasma plume) by being dissociated from the target and ablated out with stoichiometry as in the target. During this stage the emitted material moves toward the substrate according to the laws of gas-dynamic [72]. Then, the material is deposited as a thin film on the substrate (Fig. 2.8.) This process can occur in an ultra-high vacuum or in the presence of background gas, such as oxygen which is commonly used when depositing oxides to fully oxygenate the deposited films.

2.4.2 Chemical deposition

A fluid precursor undergoes a chemical change at the solid surface, leaving a solid layer. An everyday example is the formation of soot on a cool object when it is placed inside a flame. Since the fluid surrounds the solid object, the deposition takes place on every surface with little regard to direction.

2.4.2.1 Chemical vapor deposition

Chemical vapor deposition or CVD is a generic term for a group of processes that involve deposition of a solid material from a gaseous phase and is similar in some respects to PVD. CVD is a chemical process used to produce high-purity, high-performance solid materials. It is often used in the semiconductor industry to produce thin films. In this process, reactive precursors are vaporized into a carrier gas stream. The resulting vapor feed is directed to the hot glass surface or substrate, where it reacts to form a ceramic coating. In a typical CVD process, the substrate is exposed to one or more volatile precursors which react and/or decompose on the substrate surface in order to produce the desired deposit. Frequently, volatile by-products are produced and then removed by gas flow through the reaction chamber (Fig. 2.9).

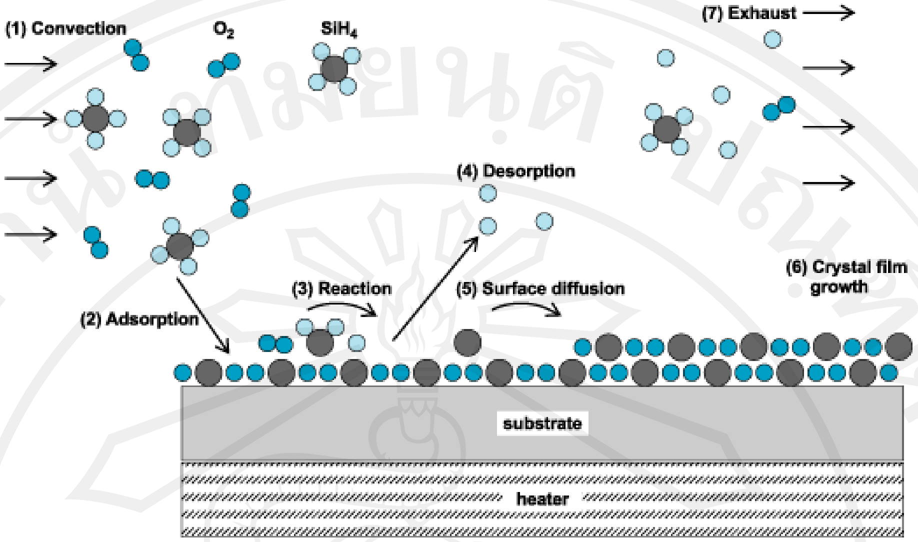

Figure 2.9 Sequence of steps involved in the deposition and crystal growth of a solid material (SiO_2) from gas precursors (SiH_4 + $2O_2$) on the surface of a heated substrate (Si) by chemical vapour deposition process [74].

2.4.2.2 Sol-gel

The sol-gel process is a wet-chemical technique popular in the field of materials science and ceramic engineering. The sol-gel process allows synthesizing ceramic materials of high purity and homogeneity by means of preparation techniques different from the traditional process of fusion of oxides. This process occurs in a liquid solution of organometallic precursors such as TMOS, TEOS, Zr(IV)-Propoxide, Ti(IV)-Butoxide, etc., which, by means of hydrolysis and condensation reactions, leads to the formation of a new phase (sol). The sol is made of solid particles of a diameter of a few hundredth of nm suspended in a liquid phase. Then the particles are condensed in a new phase (gel) in which a solid macromolecule is immersed in a liquid phase (solvent).

All the techniques mentioned above are comparative in some aspects and are summarized in Table 2.2. For comparative purposes reference is also made to the sol-gel process. The sol-gel process clearly has disadvantages associated with the vapor phase deposition of thin films and related compositions. The sol-gel process with a high degree of control chemical composition and low cost processing has the potential to eliminate some of the disadvantages to produce highly stoichiometric films with the commercial advantage of high output and low cost [1]. Sol–gel coating techniques is a popular means of fabricating PZT films and used in this work.

2.5 Sol-gel processing

The use of sol-gel technology extends back in the history. One of the earliest reports on the use of sol-gel process is German form 1983 by Geffcken and Berger [75], describing a method for preparing single oxide coatings from metal alkoxide solutions. Commercial production of sol-gel derived films began in the 1950s. Film compositions based on SiO_2 and TiO_2 were used for rear-view mirrors, anti-reflective (AR) coating and sun-shielding windows [76]. Alongside, nuclear industry utilized the sol-gel process to produce spherical particles of radioactive oxides for use in fuel cells [77]. In 1969 Dislich patented a process proliferated in1977 with the reports by Yoldas [78] on the direct preparation of SiO_2 based glass monoliths. Now, the sol-gel process has been applied to a huge range of glass and ceramics compositions for numerous applications.

Although the sol-gel processing of materials has been studied for more than 100 years [79], the use of related chemical solution deposition (CSD) techniques for the preparation of ferroelectric thin films has come out later. The process involves the synthesis of a multicomponent solution which may be applied as a coating onto a substrate with the formation of the preferred crystalline phase induced by heat treatment [78-81]. A variety of solution synthesis methods have been developed, the vast majority of which are based on metallo-organic precursors. Today, three general classes of approaches are extensively utilized, including sol-gel, chelate (molecularly modified precursors), and metallo-organic decomposition (MOD). Notable studies of CSD began with Fukushima et al. [82] and Budd and his colleagues [83, 84]. These investigations are significant as they firstly demonstrated the possibility of attaining the bulk material properties associated with ferroelectric compositions in the form of thin film. Their studies and the additional work of other researchers on chemical preparation of materials brought rapid, worldwide growth of this field and stimulated further investigation of ferroelectric thin film devices. Today, commercially available devices include decoupling capacitors [85], smart cards based on ferroelectric random access memory (FeRAM) and microelectromechanical systems (MEMS).

In addition, one advantage of sol-gel process is versatility which enables the fabrication of various structures, including small monoliths, fibers and powders. The most obvious use for sol-gel technology is probably the fabrication of thin films which are easily formed from a sol by spin-on or dip-coating techniques. The sol-gel process is favored over competing technologies as it offers such benefits as high volume output at low cost, low temperature processing and almost limitless range of film compositions. As a result, this versatile process is exploited to produce thin layers in a number of fields, such as optical coating for window glass to control reflectance, transmission and absorption, anti-reflective (AR) coatings to improve the efficiency of solar cells, superconducting ceramics, protective coatings and a large range of ferroelectric oxides.

2.5.1 Sol-gel chemistry

The term sol-gel processing applies to a system in which a sol, a dispersion of colloids in a liquid, is converted to a gelled state [86]. There are essentially two classifications for sol-gel systems:

1) Colloidal systems in which an aqueous suspension of metal oxide or hydroxide particles is aggregated to form a gel.
2) Polymeric systems in which a gel network is obtained by inorganic polymerization of molecular precursors.

The processes based on the colloidal former system are generally used for preparation of powders and are not considered in this thesis. In polymeric systems, numerous alcohols are employed as solvents. For ferroelectric thin-film fabrication, 2-methoxyethanol ($CH_3OCH_2CH_2OH$) has been used most extensively. The starting reagents are typically alkoxide compounds, and the key reactions causing the formation of a metal atom bonded to an alkyl group via oxygen and the metal-oxygen-metal (M-O-M) network that is eventually formed are hydrolysis and condensation of metal-organic precursors.

Hydrolysis:

$$M(OR)_x + H_2O \rightarrow HO-M(OR)_{x-1} + ROH \qquad \textbf{(2.3)}$$

$$M(OR)_x + xH_2O \rightarrow M(OH)_x + xROH \qquad \textbf{(2.4)}$$

Polycondensation reaction of such species results in the growth of inorganic polymers or precipitation of metal hydroxides.

Condensation (alcohol elimination):

$$(RO)_{x-1}M-OH \;+\; RO-M(OR)_{x-1} \rightarrow (RO)_{x-1}M-O-M(OR)_{x-1} \;+\; ROH \quad \textbf{(2.5)}$$

Condensation (water elimination):

$$(RO)_{x-1}M-OH \;+\; HO-M(OR)_{x-1} \rightarrow (RO)_{x-1}M-O-M(OR)_{x-1} \;+\; H_2O \quad \textbf{(2.6)}$$

Another key reaction associated with the use of this solvent is the alcohol exchange reaction, which results in reduced hydrolysis sensitivity of the starting reagents used frequently in the production of PZT films, such as zirconium *n*-propoxide and titanium *i*-propoxide. This reaction is represented below.

Alcohol exchange:

$$M(OR)_x \;+ xR'OH \rightarrow M(OR')_x \;+\; xROH \quad \textbf{(2.7)}$$

Where OR is a reactive alkoxy group, and OR' is the less reactive methoxyethoxy group. As written in the reaction, complete exchange has occurred. 2-methoxyethanol represents a chelate-forming, non-bridging bidentate ligand (Fig. 2.10). Thus, 2-methoxyethanol is not a simply solvent in these processes. In addition to the alcohol exchange reaction, 2-methoxyethanol was also found to be beneficial in the dissolution of carboxylate precursors, such as lead acetate. In this case, by refluxing the lead acetate precursor in 2-methoxyethanol, one of the acetate groups is replaced, resulting in the formation of the soluble mixed-ligand precursor $Pb(OOCCH_3)(OCH_2CH_2OCH_3)\cdot 0.5H_2O$ [87]. Typically, carboxylate compounds for lead are employed because of the instability of lead alkoxides and their limited commercial availability.

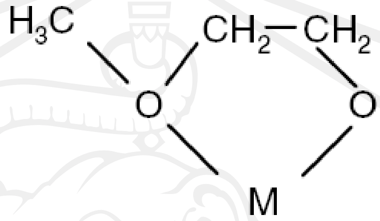

Figure 2.10 An example of metallo-organic precursors commonly used in the fabrication of ferroelectric perovskite thin films: schematic of the 2-methoxyethoxy ligand bonded to a metal center.

The steps in Fig. 2.11 represent (1) dissolution of the lead source with the formation of the mixed-ligand precursor noted above; (2) alcohol exchange through reflux and distillation to form a titanium precursor that is less susceptible to hydrolysis; (3) combination of the solutions with the possible formation of a mixed-metal compound and (4) partial hydrolysis of the solution for the formation of larger oligomeric species. Gelation occurs in polymeric sols through the continued growth of dispersed intermediate species to form a three dimensional network. The gel point is the time at which a macromolecule appears to encompass the entire sol, experimentally observed as a sharp increase in viscosity. The gel may be consisting of continuous solid and liquid phase of colloidal dimensions [86].

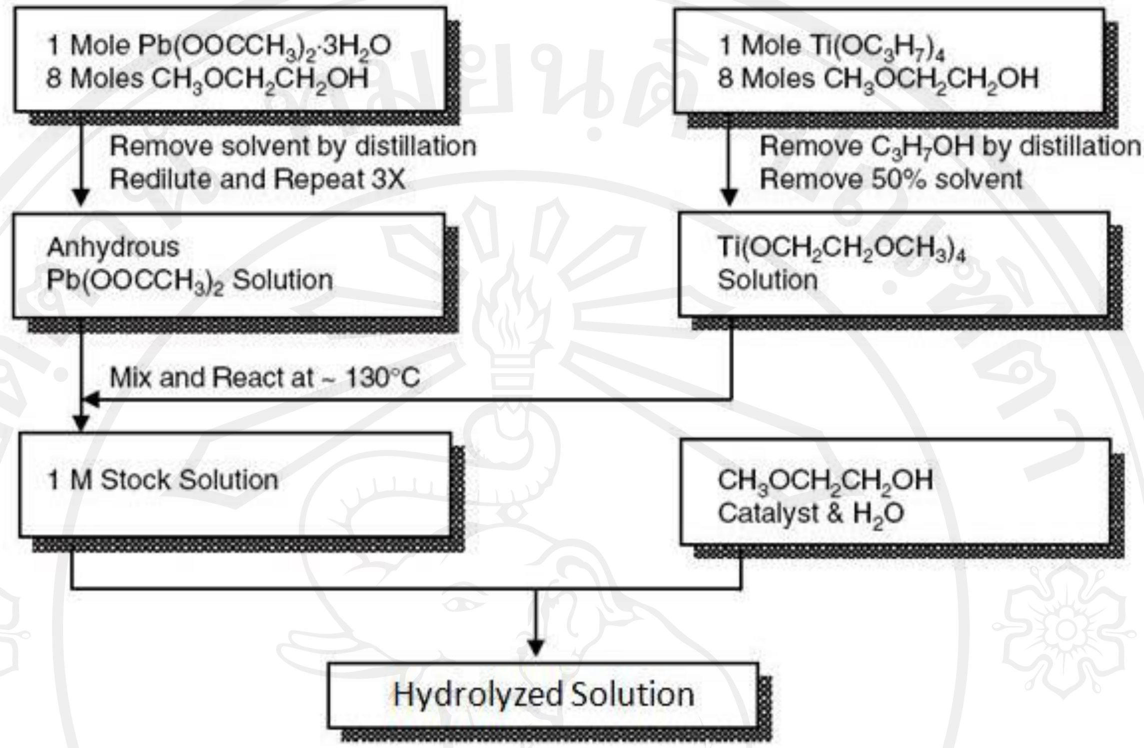

Figure 2.11 A flow diagram for a representative 2-methoxyethanol process illustrated for the preparation of $PbTiO_3$ [86].

Drying gels by evaporation results in the formation of a xerogel, a porous and generally amorphous solid. A large shrinkage occurs due to the capillary pressure of the drying front within the gel. Drying under hypercritical conditions eliminates the liquid/vapor interface and avoids drying shrinkage. The resulting highly porous solid is termed an aerogel. Dense ceramics are obtained by firing the dried gel. Due to the chemical homogeneity and high surface area of gel, crystallization and sintering occur at relatively low temperatures.

Table 2.2 Comparison of important process parameters of fabrication routes for thin films of $PbTiO_3$ and PZT [1].

Stage	Process	Composition control	Annealing temperature (°C)	Deposition rate (nm/min)	Cost
Vapor	Evaporation	Poor	500-700	10-500	high
Vapor	RF sputter	Poor	500-750	1-5	high
Vapor	DC magnetron sputter	moderate	500-750	2-20	high
Vapor	RF magnetron sputter	moderate	500-700	2-10	high
Vapor	Ion beam sputter	moderate	500-700	3-10	high
Vapor	Laser deposition	moderate	500-800	20-100	high
Vapor	MOCVD	moderate	600-800	10-100	high
Solution	Sol-gel	good	500-700	Multiple coats	low

Advantages of this method include excellent control and reproducibility of the process chemistry and low aging rates for non-hydrolyzed solutions. A common disadvantage of the method is the comparatively involved chemical procedures, including several reflux and distillation steps. Another disadvantage is the toxicity of the most commonly used solvent, 2-methoxyethanol.

2.6 Electrical properties of PZT

Due to its outstanding ferroelectric properties, even for polycrystalline materials, PZT has been regarded as the best ferroelectric and piezoelectric material for a long time [88, 89]. Furthermore, ferroelectric PZT shows anomalous, high piezoelectric and dielectric properties in the vicinity of an MPB. Many devices are based on compounds with compositions near the MPB, where the capability of polarization and piezoelectric coupling coefficient are improved [90, 91]. Consequently, it is important to know the background of some important electrical properties.

Structural symmetry of a crystal depends on its lattice structure and affects both physical and electrical properties of the crystal, such as dielectric, elastic, piezoelectric, ferroelectric and nonlinear optical properties. This theory corresponds to thousands of crystals in nature. All crystals can be divided into 32 different classes or point groups according to their crystallographic symmetry as shown in Fig. 2.12. The point groups can be divided largely into two classes, the centers of symmetry (11) and the non-center of symmetry (21). Out of the 21 point groups which have the non-center of symmetry, 20 point groups generate positive and negative charges on surfaces when stresses are applied. This phenomenon is known as piezoelectricity. Piezoelectricity was discovered in 1880 by Pierre and Jacques Curie during their research on the effect of pressure on generation of charge in quartz. The name “piezo” is derived from the Greek, meaning “to press.” Hence, piezoelectricity is defined as the ability of certain crystalline materials to develop an electrical charge proportional to an applied mechanical stress or vice versa [89]. Out of the 20 point groups with the piezoelectric effect, 10 point groups are designated as pyroelectric, which is an unusual characteristic of being permanently polarized within a given temperature range. Unlike the general piezoelectric classes which create a polarization under stress, the pyroelectrics develop this polarization spontaneously and form permanent dipoles in the structure. This polarization also changes with temperature, hence the term pyroelectricity (the name “pyro” is derived from the Greek, meaning “fire”).

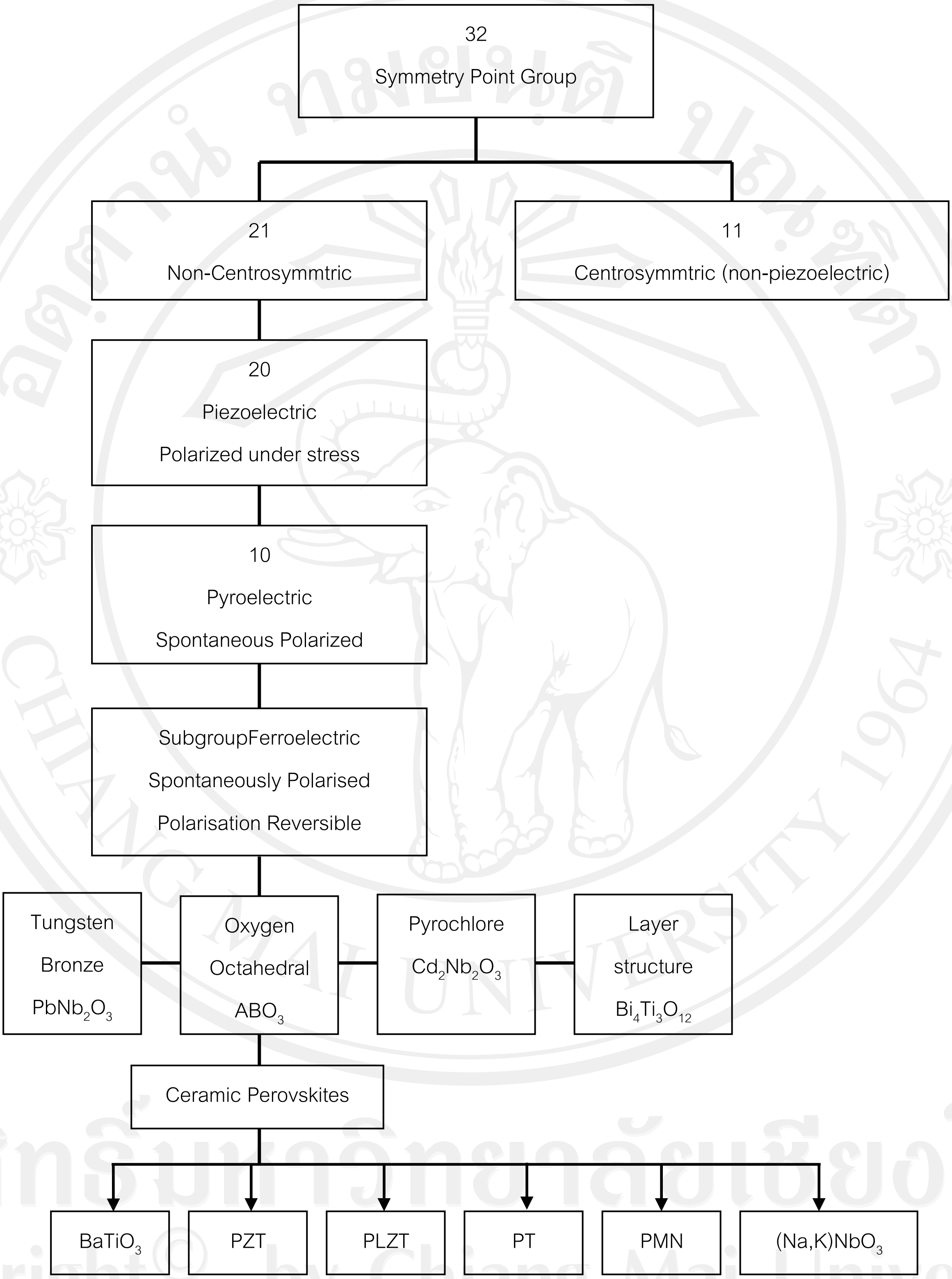

Figure 2.12 Classification scheme for the 32 crystallographic point groups [1].

The subgroup of the spontaneously polarized pyroelectrics belongs to a special category known as ferroelectrics. Similar to pyroelectrics, ferroelectrics possess spontaneous dipoles; however, unlike pyroelectric, these dipoles are reversible by an electric field of some magnitude less than the dielectric breakdown of the material itself.

2.6.1 Piezoelectricity

Piezoelectricity is the ability of certain crystalline materials to develop an electrical charge proportional to an applied mechanical stress or vice versa [89].There are two different piezoelectric effects: direct and indirect. In direct piezoelectric effect, ceramics with certain structure become electrically polarized when the stress is applied (Fig. 2.13).

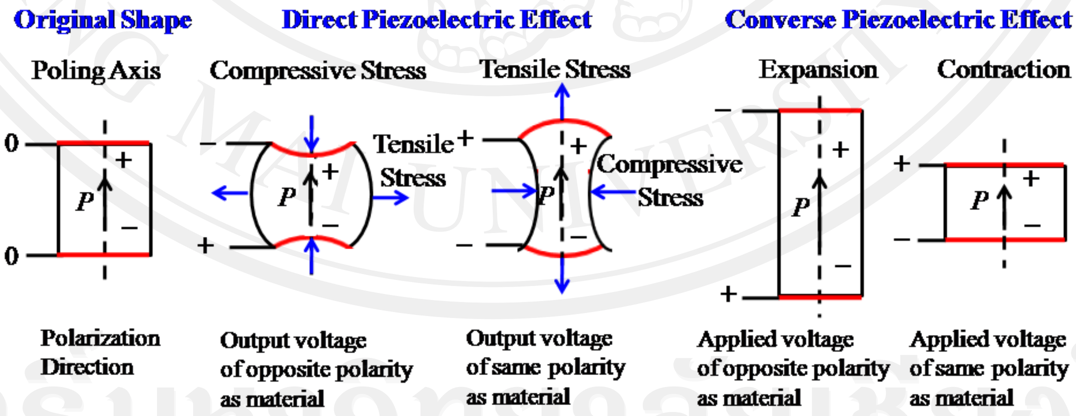

Figure 2.13 Schematic representation of piezoelectric behavior of direct and indirect (converse) effect [89].

For indirect (or converse) piezoelectric effect, the geometric strain (deformation) is produced by applying a voltage. The piezoelectric effect in crystals is result from the creation of electric dipole moments (polarization) and the establishment of electric field across the specimen by applying external forces. All ferroelectric materials are potentially piezoelectric.

2.6.2 Dielectric

A response of materials to an electric field is described as dielectric and can be advantageous even when no charge is transferred. Dielectric materials possess a large energy gap between a valence and conduction bands, and thus, have a high electrical resistivity. Two important applications of dielectric materials are electrical insulators and capacitors. Consider a vacuum capacitor consisting of a pair of parallel electrodes. The familiar parallel plate capacitor equation with free space as an insulator is given below (2.8).

$$C = \frac{\varepsilon_0 A}{d} \qquad \textbf{(2.8)}$$

Where ε_0 is the absolute permittivity; A is the plate area; and d is the separation between the plates. Given a material medium between the plates, then the capacitance or charge storage ability per unit voltage are increased by a factor of ε_r, the dielectric constant of the medium or its relative permittivity. The increase in capacitance is due to the polarization of the medium in which positive and negative charge are displaced with respect to their equilibrium positions. The opposite surfaces of the dielectric medium acquires opposite surface charge densities that are related to the degree of polarization in the material. An important concept in dielectric theory is an electric dipole moment p, a measure of the electrostatic effects of a pair of opposite charges $+Q$ and $-Q$ separated by a finite distance a (Fig. 2.14).

$$p = Qa \tag{2.9}$$

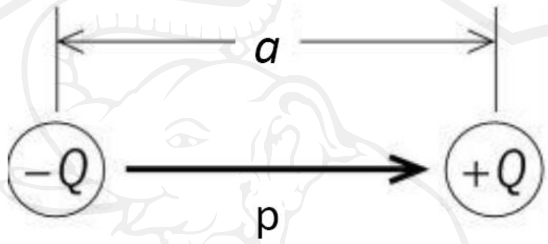

Figure 2.14 The definition of electric dipole moment [92].

Although the net charge is zero, this entity still gives rise to an electric field in space and also interacts with the field from other sources. The relative permittivity is a material property that is frequency dependent. Some capacitors are designed to work at low frequencies, whereas others have a wide frequency range. Furthermore, while they are regarded as energy storage devices, all practical capacitors exhibit some losses when used in an electric circuit. These losses are not different from I^2R losses in a resistor carrying a current. The power dissipation in a practical capacitor depends on the frequency, and for some applications it can be an important factor. A defining property of a dielectric medium is not only its ability to increase capacitance but also its insulating behavior or low conductivity which prevents the charges from being conducted from one plate of the capacitor to the other through the dielectric.

Dielectric materials often serve to insulate current-carrying conductors or conductors at different voltages. Therefore, even air can be used as an insulator between high-voltage conductors. When the electric field inside an insulator exceeds a critical field called the dielectric strength, the medium suffers dielectric breakdown and a large discharge current flow through the dielectric. Approximately 40 percent of utility generator failures are associated with insulation failures. Dielectric breakdown is probably one of the oldest electrical engineering problems which has been most widely studied and never explained fully [92].

2.6.2.1 Relative permittivity

Consider a parallel plate capacitor with vacuum as the dielectric medium between the plates, as shown in Fig. 2.15(a). The plates are connected to a constant voltage supply V. Given Q_0 is the charge on the plates, this charge can be easily measured. The capacitance C_0 of the parallel plate capacitor in free space (Fig. 2.15(a)) is defined by

$$C_0 = \frac{Q_0}{V} \tag{2.10}$$

The electric field, directed from high to low potential, is defined by the gradient of the potential $E = -dV/dx$. Thus, the electric field E between the plates is just V/d, where d is the separation of the plates. Therefore, the charge stored in the capacitor is $Q_0 = \varepsilon_0 AE$, and if a homogeneous dielectric is introduced between the plates keeping the potential constant the charge stored is given by

$$Q = \varepsilon_0 \varepsilon_r A E \tag{2.11}$$

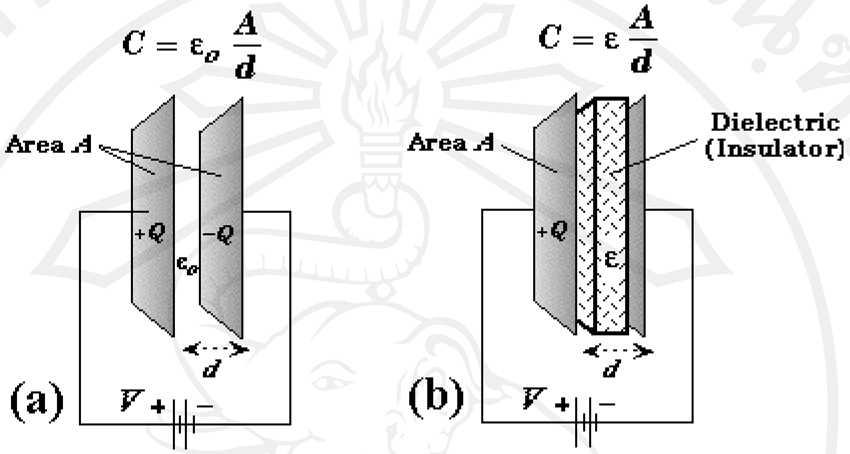

Figure 2.15 Parallel plate capacitor with (a) free space between the plates and (b) insertion of dielectric medium between the plates [92].

Consider what happens when a dielectric slap is inserted into this parallel plate capacitor, as shown in Fig. 2.15(b), with *V* kept constant. During the insertion, there is an external current flow, indicating that the additional charge is being stored on the plates. The charge on the electrodes increases from Q_0 to Q. The extra charge is $Q - Q_0$. Because there is the greater amount of charge stored on the plates, the capacitance of the system in Fig. 2.15(b) is now larger than that in Fig. 2.15(a).

Due to $E = V/d$ then the charge stored in the capacitor is $Q = \varepsilon_0 \varepsilon_r AV/d$, when considering to capacitance, since the charge is $Q = CV$. Therefore, the capacitance of parallel plate with dielectric capacitor is defined by

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \tag{2.12}$$

The increase in the stored charge is due to the polarization of the dielectric by the applied field [92].

2.6.2.2 Dielectric loss

Some energy is lost as heat when a dielectric material is polarized in an alternating electrical field. The fraction of the energy lost during each reversal is termed dielectric loss (tanδ). The energy loss is due primarily to two factors: current leakage and dipole friction. The loss due to current leakage is low if the electrical resistivity is high. Dipole friction occurs when reorientation of dipoles is difficult, as in complex organic molecules. The greatest loss occurs at the frequencies where the dipoles almost cannot be reoriented. At lower frequencies, losses are low because the dipoles have sufficient time to move. At higher frequencies, losses are also low because the dipoles do not move at all.

2.6.3 Ferroelectricity

Most pyroelectric crystals exhibit a spontaneous polarization (P_s) in a certain temperature range, and the direction of (P_s) can be reversed by an external electric field. Ferroelectricity was discovered in 1921 by Valasek [93]. Rochelle salt was the first material found to possess ferroelectric properties such as reorientable, spontaneous polarization when cooled below a transition temperature (Curie temperature; T_c). Many ferroelectrics are low temperature modifications instead of high temperature and a higher symmetry structure (prototype) which has no spontaneous polarization. This prototype is also called paraelectric. In the ferroelectric phase, modifications to cation and anion positions occur and give relative displacements of ions inside the unit cell, resulting in reversible spontaneous dipole moments.

Another important characteristic of ferroelectrics is the temperature of the phase transition, the Curie point (T_c). When temperature decreases to the Curie point, a ferroelectric crystal undergoes a structural phase transition, from the paraelectric phase to the ferroelectric phase. Ferroelectricity is only exhibited when the temperature decreases below T_c.

2.6.3.1 Ferroelectric phase and domain

Ferroelectricity is exhibited in certain crystal structures which can be polarized even in the absence of applied field. This polarization can be reoriented or reversed fully by applying an electric field. The complete reversal of spontaneous polarization is termed switching. Ferroelectrics may exhibit one or more ferroelectric (polar) phases (Fig. 2.16) that show a domain structure in which the individual domain states can be reoriented by an applied field. In a ferroelectric crystal there are usually many domains whose regions are uniform polarization. Within each individual domain, all the electric dipoles are aligned in the same direction. These domains are separated by interfaces called domain walls [94]. Since domain walls differ from the perfect crystal, there is a certain amount of energy (W_{dw}: domain wall energy) associated with domain walls in addition to the elastic energy (W_e). From energy considerations in real materials, domain patterns depend on many factors, including the existing defect structure and concentration, stress and electric history, boundary conditions, temperature relative to T_c and even the history of crystal preparation [95, 96].

From a phenomenological point of view, the origin of a ferroelectric domain is the polydomain system in a state of minimum free energy. From a microscopic viewpoint, domains are attributed to the change in the electrostatic forces acting on the face of crystal because of the spontaneous polarization that occurs as the crystal goes through the paraelectric-ferroelectric phase transition.

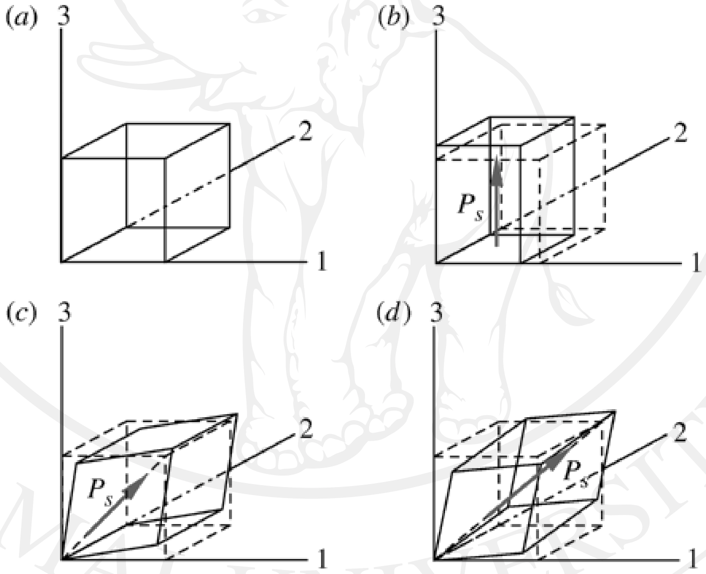

Figure 2.16 Unit cells of the four phases: (a) cubic, (b) tetragonal, (c) orthorhombic and (d) rhombohedral. Dotted lines in (b), (c) and (d) indicate the original cubic cell). Arrows indicate the direction of the spontaneous polarization (Ps) in each phase [96].

Figure 2.17 shows 180° domain formation which minimizes the electrostatic energy of the system.

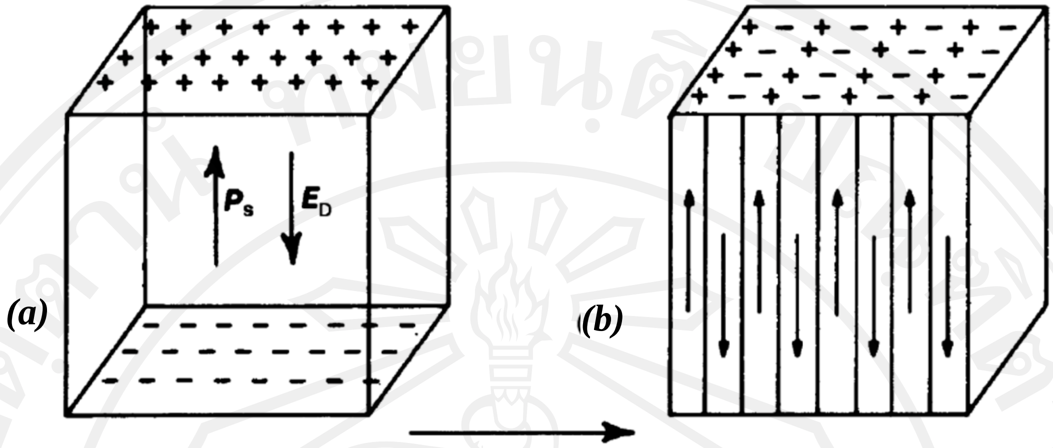

Figure 2.17 (a) Surface charge and depolarizing field (E_D) associated with spontaneous polarization (Ps) and (b) is a formation of 180° domains to minimize electrostatic energy [39].

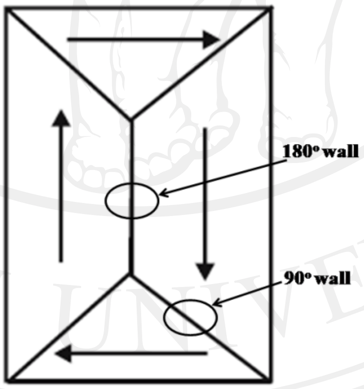

Figure 2.18 A schematic illustration of 180° and 90° domain walls [97].

Defects and internal stresses must be also considered for a crystal that exhibits piezoelectricity in the paraelectric state [94]. The presence of mechanical stress in a crystal results in the development of non-180° domain walls configured to minimize the strain as shown in Fig. 2.18. The structure of a ferroelectric domain depends on the structure of a crystal. In a ferroelectric crystal, when the spontaneous polarization occurs from the prototype phase, the variety of domain patterns and the number of types of domain walls depend on the number of orientations of the dipole moment.

2.6.3.2 Polarization switching and hysteresis loop

A single domain can be gained by domain wall motion made possibly by the application of an appropriate electric field. A strong applied field could lead to the reversal of polarization in the domain, a phenomenon known as polarization (or domain) switching. Polarization switching is characteristics of ferroelectricity which can be observed by measuring the hysteresis polarization as a function of applied electric field called *P-E* hysteresis loop. The hysteresis loop is typically observed using a simple circuit described by Sawyer-Tower [98]. The behavior corresponds to the segment (OA) of *P-E* loop (Fig. 2.19). As the electric field strength increases, a number of the domains with the opposite polarization direction are switched towards the field direction, producing a rapid increase in polarization (segment AB). When all the domains are aligned in the field direction, it reaches a saturation state (BC). At this saturation state, properly oriented crystals are composed of a single domain. As the field strength decreases, the polarization will decrease (BD) but does not bounce back to zero. When the field is reduced to zero, some of domains will remain aligned, and the crystal exhibits a remanent polarization (P_r). The extrapolation of the linear segment BC of the hysteresis loop back to the polarization axis (CBE) represents the value of the spontaneous polarization (P_s), in the case of an appropriately oriented, fully poled crystal.

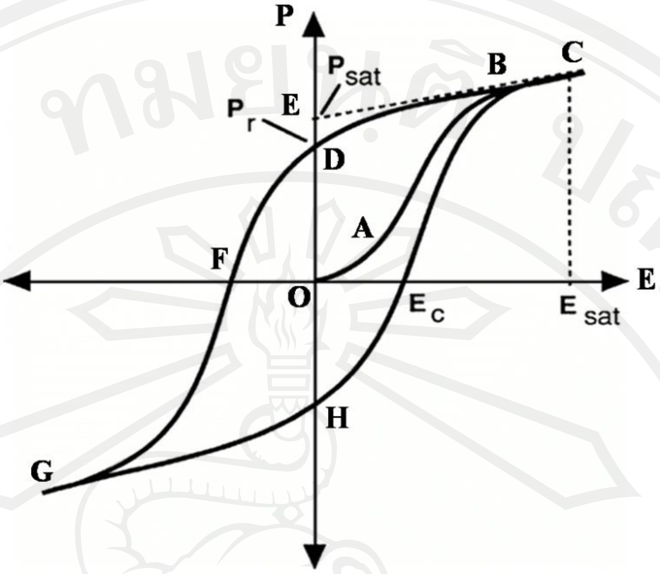

Figure 2.19 A typical P-E hysteresis loop in ferroelectrics [94].

The remanent polarization in a crystal cannot be removed until the applied field in the opposite direction reaches a certain value (at the point F in Fig. 2.19). The strength of the field required to reduce the polarization back to zero is called the coercive field strength (E_c). Further, the increase of the field in the negative direction will cause and alignment of the dipole in this direction and the cycle can be completed by reversing the field direction once again. Thus, the relation between P and E is represented by a hysteresis loop (CDFGHC) as shown in Fig. 2.19 [94].

2.6.4 Fatigue characteristic

Ferroelectric fatigue describes that the change of the hysteresis loop depends on the number of switching cycles. The core effect of fatigue is a loss in the remanent polarization (P_r) and in the saturation polarization (P_{sat}) values transmitting electric field [90]. Fig. 2.20 shows the scheme of the polarization decay in a ferroelectric material as a function of the number of cycles and also the corresponding evolution of the hysteresis loops.

Fatigue behavior is usually illustrated by plotting the remanent polarization (P_r) as a function of the numbers of switching cycles (N), as shown in Fig. 2.21. There are three stages in this plot: the slow fatigue stage (up to 10^5 switching cycles), the logarithmic stage (around 10^6 switching cycles) and the saturated stage (after 10^8 switching cycles) [99]. Nevertheless, it has been observed that the remanent polarization was partially restored to some extent in some samples at high switching cycle numbers. The detailed profile of this curve depends strongly on the material, the sample preparation method, the type of electrode, and the experimental conditions under which fatigue measurements are conducted [100].

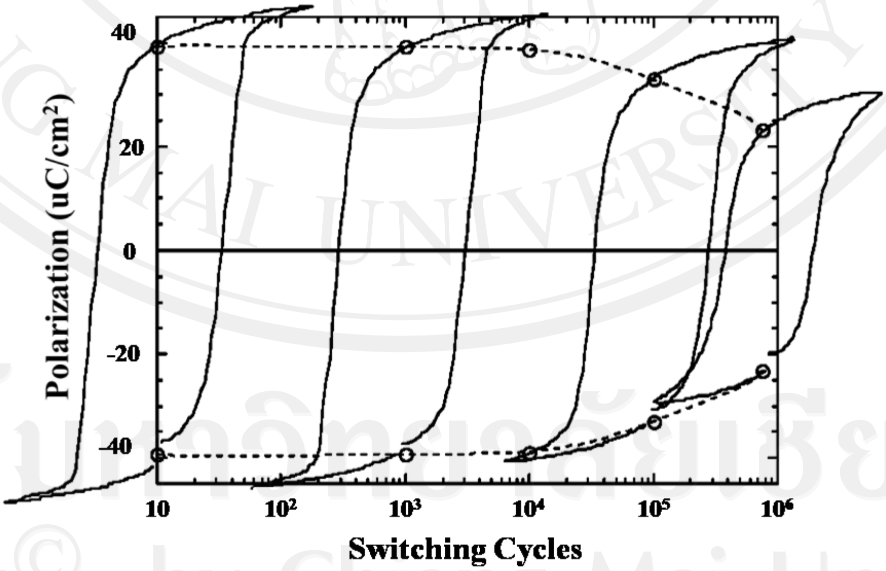

Figure 2.20 A schematic illustration of polarization decay as a function of the number of switching cycles [99].

Fatigue is generally the result of charge injection and the accumulation of space charge that pins switching [100]. However, the mechanisms of ferroelectric fatigue are largely known today. During the past 50 years, the influence of various conditions (e.g. temperature, frequency, doping of the ferroelectric material, type of electrode and characteristics of the external electric field on electrical fatigue) has been explored. These parameters have been exploited to improve the fatigue resistance, as shown in the following section.

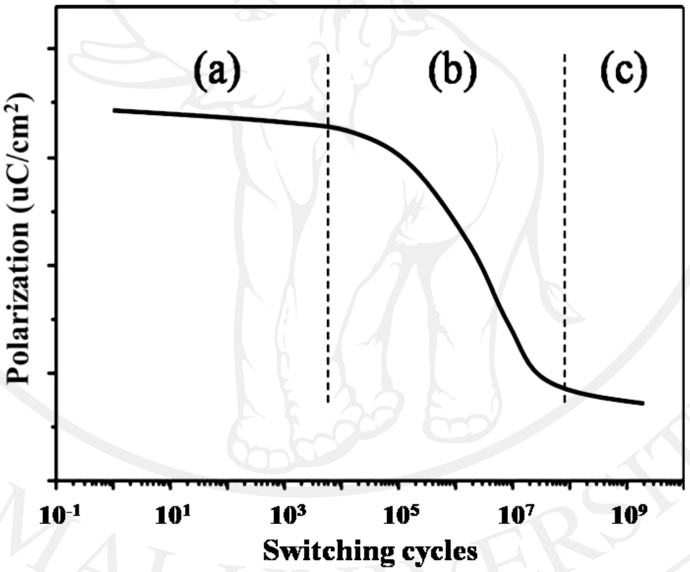

Figure 2.21 Evolution of polarization with the number of switching cycles: (a) the slow fatigue stage, (b) the logarithmic stage and (c) the saturated stage [101].

2.6.4.1 Factors influencing of fatigue behavior

Many have studied the influencing factors to improve fatigue resistance in ferroelectric materials. These studies can be summarized in three major factors.

2.6.4.1.1 Compositional changes and doping

Most material properties depend upon the composition and effect of doping. Currently studied ferroelectrics are generally solid solutions of two compounds of different characteristics. Jiang et al. [102] investigated the effect of composition on electric fatigue of La-doped lead zirconate titanate (PLZT) ceramics. They reported that bulk PLZT of rhombohedral symmetry showed little or no fatigue compared with those of tetragonal or orthorhombic symmetry (Fig. 2.22). They also revealed that switching by an electric field took place more easily in a ferroelectric rhombohedral phase, indicating that internal stresses are smaller for rhombohedral structure during the switching process. They attributed the reasons for fatigue to the pinning of domains by space charges or injected carriers or to microcracks arising from large incompatible stresses between grains and resultant permanent damages.

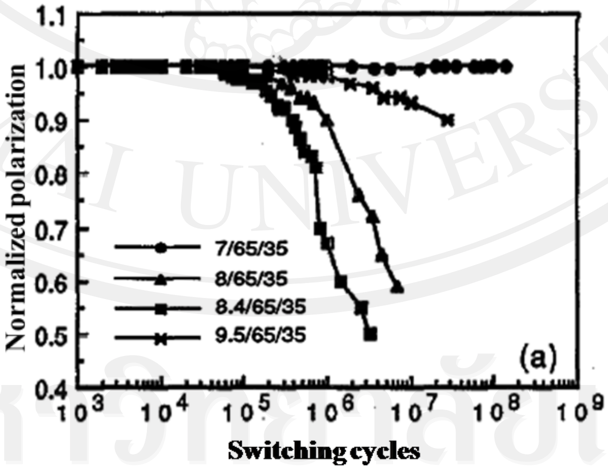

Figure 2.22 Normalized polarizations as a function of the switching cycles of PLZT ceramics with composition *x*/65/35 [102].

It is well known that the electrical properties of materials can be modified by ion substitution, which is termed doping. Depending on their location in the crystalline structure, the dopants may be classified as donors, acceptors or isovalent substituents. Some of the effects of donor doping vital for polarization switching processes and fatigue are listed below:

- reduced oxygen vacancy concentration
- high remanent polarization and low coercive field
- relatively square loops
- easy poling
- increased domain wall mobility

Reduced oxygen vacancy concentration and easier domain reorientation have been presented as the key elements for improved electrical properties in ferroelectric bulk ceramics [89]. Generally speaking, oxygen vacancies, the most mobile species in perovskite structure, contribute to fatigue of ferroelectric materials. Therefore, the studies on controlling oxygen vacancies by doping or changing processing conditions and compositional studies have provided improvements in fatigue behavior.

2.6.4.1.2 Use of oxide electrodes

The influence of electrodes was found to be crucial to the fatigue endurance of ferroelectric, especially for thin films. Another method to improve fatigue behavior is the use of oxide electrodes (e.g. RuO_2, IrO_2 and $SrRuO_3$) which suppresses the detrimental effects of oxygen vacancies. When these oxide electrodes were utilized in place of metal electrodes, the polarization fatigue could be reduced as shown in Fig. 2.23.

There is clearly an advantage of using oxide electrodes with regard to improving ferroelectric fatigue behavior, for oxide electrodes may act as sinks for the oxygen vacancies which reduce fatigue.

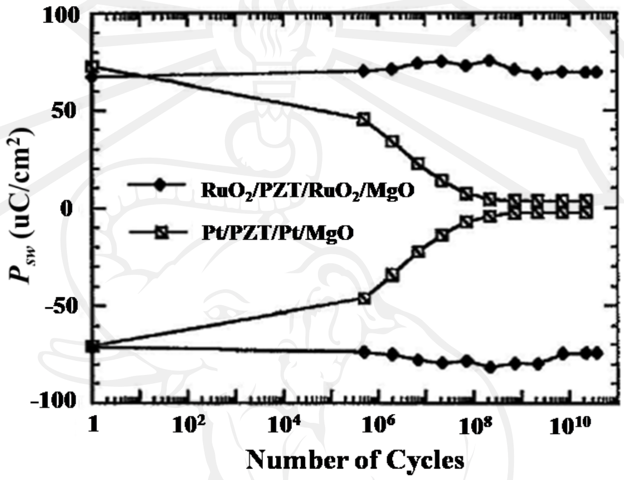

Figure 2.23 Fatigue behaviors of Pt/PZT/Pt/MgO and RuO$_2$/PZT/RuO$_2$/MgO capacitors. The fatigue tests were performed at 500 kHz [103].

2.6.4.1.3 Alternative ferroelectric materials

The bismuth layered perovskite materials such as SrBi$_2$Ta$_2$O$_9$ (SBT) and doped-Bi$_4$Ti$_3$O$_{12}$ (doped-BIT) show high fatigue endurance (up to 10^{12} switching cycles) [104], and thereby studied by many researchers.

The better fatigue endurance in layered perovskite ferroelectrics compared to perovskite ferroelectric PZT is due to a relatively smaller magnitude of ferroelectric polarization and possibly a lower accumulation of oxygen vacancies at the electrode/film interface.

2.6.4.2 Polarization fatigue mechanisms

The presently considered fatigue mechanisms in ferroelectrics include;

- formation of a surface layer [105]
- pinning of domain walls by defects segregated in the wall region [106]
- clamping of polarization reversal by volume defects [90]
- suppression of nucleation of oppositely oriented domains at the surface [107]
- damage of electrode/film interface [108]

The role of oxygen vacancies in the fatigue process of ferroelectric materials is discussed below together with the models of domain wall pinning and clamping.

2.6.4.2.1 Possible roles of the oxygen vacancies

Several models of the polarization fatigue in ferroelectric materials are based on the observation that oxygen vacancies accumulate at the film/electrode interface during field cycling. Scott et al. [105] suggested that oxygen deficient regions grow into the bulk, effectively screening a part of the film from the applied field and leading to polarization loss. Another model proposed that the polarization loss is due to structural damage at the film/electrode interface due to entrapped oxygen vacancies. Mihara et al. [109] also confirmed evidence for the creation of oxygen deficient layers at film/electrode interfaces in $Pb(Zr_{0.4}Ti_{0.6})O_3$ thin films fatigued by electric field cycling. However, their results suggested that the fatigue is due to pinning of domain walls by oxygen vacancies, not the presence of the interface layer.

It has been further suggested that the creation of an oxygen vacancy rich region at the film/metal electrode interface may lead to the formation of an n-type layer adjacent to the interface [105]. The presence of this layer raises the electron injection rate in the film during field cycling. The injected electronic carriers may get trapped at the domain walls, leading to domain wall pinning and polarization suppression as discussed in the section below. Another possible role of oxygen vacancies is to stabilize the trapping of electronic charges (and therefore increasing domain wall pinning) through the distortion of oxygen octahedron caused by the presence of an oxygen vacancy [110].

2.6.4.2.2 Electronic charge trapping and domain wall pinning

The model by Al-Shareef et al. [106] is based on the idea that free electronic charge carriers pin domain walls by being trapped in the domain wall region. The free electronic charges may be attracted to the domain wall regions where there is a discontinuity in polarization, thereby decreasing the energy of the walls. If the charges are trapped at these positions, the movement of the walls will be restricted. The polarization fatigue process is interpreted as a dynamic competition between domain wall pinning due to electronic charge trapping and field-assisted unpinning of the domain walls [106]. The weak fatigue in some films does not necessarily indicate the absence of domain wall pinning but rather the presence of de-pinning acting as strong as pinning. It is proposed that the unpinning may be due to a number of processes, including (i) overcoming of the pinning forces by the cycling field; (ii) de-trapping of charge carriers responsible for the domain wall pinning and (iii) recombination of photo-generated or injected carriers with the trapped charge which may unpin walls.