CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Materials technologies have shaped the various human development periods that historians have defined by the materials predominantly used in these ages, e.g. the stone age, the bronze age and the iron age. Plastics, composites and other engineered materials such as advanced ceramics identify a new age, the synthetic materials age. With the advancement of several emerging technologies such as biotechnology, nanotechnology and information technology the dawn of the 21st century will witness the emergence of the smart materials age[1].

Smart materials are functional materials designed for a variety of engineering applications, with both sensing and actuating functions. Many engineering materials can be used as sensor and actuator materials, if being properly designed, including piezoelectic ceramics, shaped-memory alloys, optical fibers, and polymers. Each of them can suit the specific potential requirements of the future intelligent materials systems[2].

PZT (lead zirconate titanate) is one of piezoelectric ceramic materials. The PZT powders can be synthesized in many different ways. The simplest way is the solid state reaction process, in which metal oxides of each component are mixed together, ball-milled and calcined[3, 4]. An alternative method is the chemical synthesis which includes coprecipitation, sol-gel, spray pyrolysis and hydrothermal processing.

These chemical methods can produce fine particles with higher homogeneity, higher purity, lower particle size with while using lower processing temperature than the solid state reaction process. The favorite wet chemical technique is the coprecipitation[5, 6]. This technique requires basical equipment, while quite good product result with controlled compositions, purity and morphology. Some parameters have to be closely controlled such as concentration ratio, pH of the solution, mixing rate and temperature during the chemical reaction.

Sol-gel technique can produce material with high homogeneity and excellent control of the composition of the final product[7-9]. However, the raw materials are expensive, and the process is not suitable for making powder. Hence, spray pyrolysis is the consequent process of coprecipitation or condensation within a droplet. Since the complete stoichiometry is formed on the droplet scale, the process is good for preparing submicron size powders[10, 11]. However, the pyrolysis temperature for PZT is 900 °C, which is higher than the volatilization temperature of lead atoms.

Hydrothermal synthesis[12-14] is a convenient process for preparing PZT or other piezoelectric powders. It is able to produce fine particles, with high homogeneity and high purity. Doping can be easily done during hydrothermal processing. The disadvantages are the high cost of the apparatus and the required pressure safety control.

This thesis concentrates on the synthesis of PZT and PLZT (lead lanthanum zirconate titanate) powders by coprecipitation and hydrothermal processing.

Coprecipitating technique can produce stoichiometric powders with high purity and fine particle size at the moderate cost. However, microscopic inhomogeneity can occur at an unsuitable precipitation rate, and the calcination step can cause agglomeration. The problem of microscopic inhomogeneity can be solved by controlling the synthesis conditions, and that of the agglomeration during calcining at high temperature can be solved by changing the route for making powders, such as changing from direct precipitation of the solution to freeze drying technique[15], which may yield better homogeneity control, higher purity, finer particle size and lower calcining temperature.

In a hydrothermal processing, a lower temperature (below 250 °C) is used at a moderate pressure in sufficient to avoid the calcination step. This relatively low temperature under moderate pressure is enough to break down the bonds within the precursor molecules, thus, avoiding agglomeration that usually occurring at the high temperature used in calcining and sintering steps of solid state reactions and other chemical processes.

After synthesis the powders will be compressed to form monolithic shapes, and poled. Dielectric constant of PZT and PLZT ceramics was measured.

1.2 CRYSTAL STRUCTURE OF PZT

1.2.1 Piezoelectricity in ferroelectric ceramics

Piezoelectricity is a property possessed by a select group of materials, was discovered in 1880 by Jaques and Pierre Curie during their study of pressure on the generation of electrical charge by crystals, such as quartz, zinc blende, and tourmaline[16]. The name “piezo” is derive from the Greek, meaning “to press” so the piezoelectricity is the generation of electricity as result of mechanical strain in crystals belonging to certain classes. The polarization being proportional to the strain and changing sign with it.

The concept of piezoelectricity begins with an understanding of the internal structure of the single crystallite. This crystallite is made up from ions that are occupied positions in a specific repeating relationship to each other and building up the structure or lattice of the crystal. The smallest repeating unit of the lattice is called the unit cell and the specific symmetry possessed by the unit cell determines that it is possible for the piezoelectricity to exist in the crystal. Furthermore, the symmetry of a crystal's internal structure is reflected in the symmetry of its external properties[16].

All crystals can be divided into 32 different classes or point groups utilizing these symmetry elements, as shown in Figure 1.1. From 32 point groups, 11 classes are centrosymmetric and 20 classes are piezoelectric[17]. Only one class is not piezoelectric because of other combined symmetry elements. A lack of a center of symmetry is all-important for the presence of piezoelectricity when one considers that a homogeneous stress is centrosymmetric and cannot produce an unsymmetrical result. Unless the material lacks a center of symmetry, whereby a net movement of the positive and negative ions with respect to each other produces electric dipoles. Furthermore for materials that are piezoelectric but notferroelectric, the stress itself is the only occurs when the dipoles are generated. The magnitude of the polarization is dependent on the magnitude of the stress and the sign of the charge produced is dependent on the type of stress.

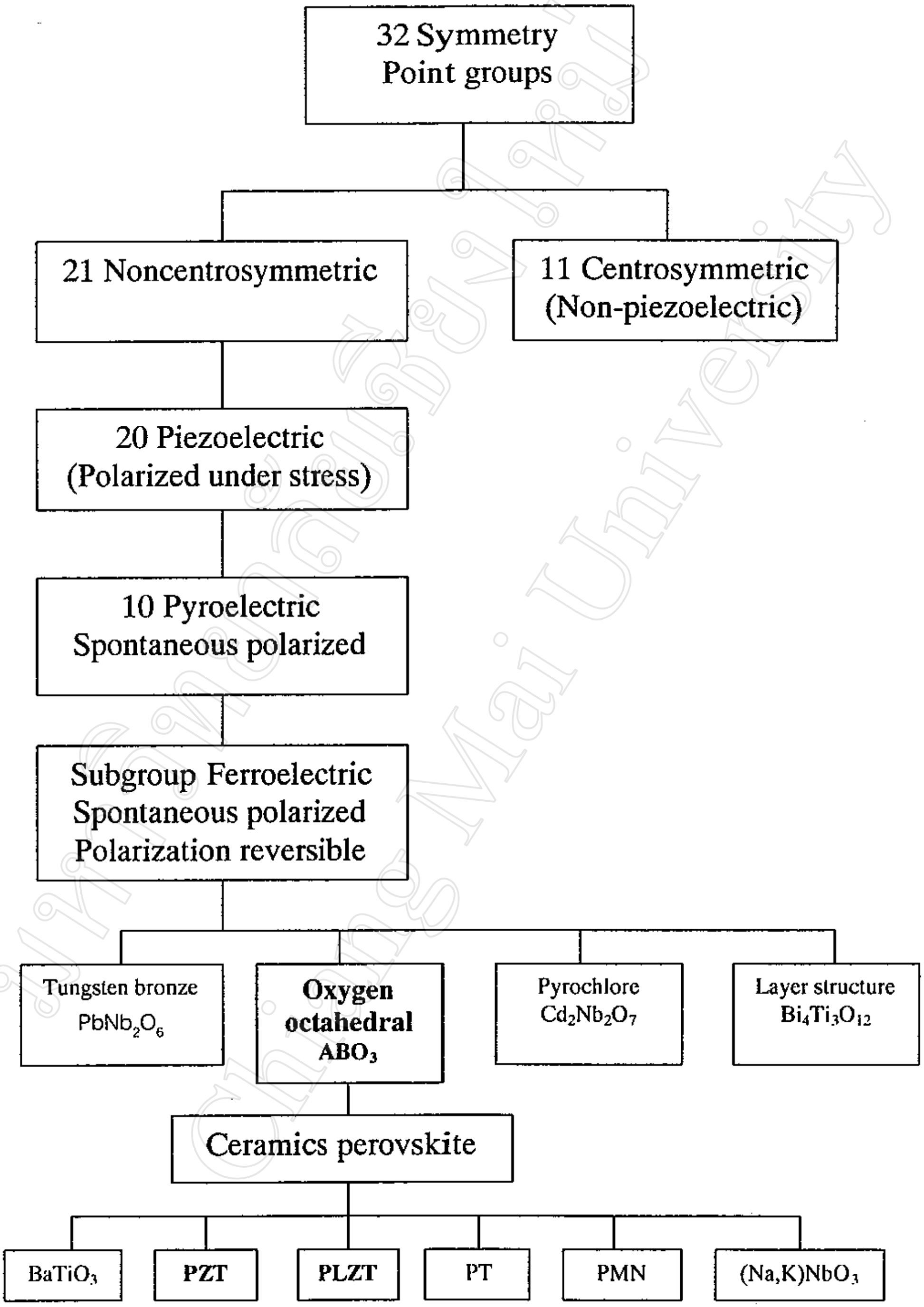


Figure 1.1 Interrelationship of piezoelectric and subgroups on the basis of symmetry[17].

Ferroelectric crystals possess regions with uniform polarization called ferroelectric domains. Within a domain, all the electric dipoles are aligned in the same direction. There may be many domains in a crystal separated by boundaries called domain walls. Adjacent domains can have their polarization vectors in antiparallel directions or at right angles to one another. The boundaries between these domains are known as 180° or 90° domain walls. A ferroelectric single crystal has multiple ferroelectric domains. A single domain can be obtained by domain wall motion made possible by the application of a sufficiently high electric field, the process known as poling. Poling is very important for the application of polycrystalline ferroelectric ceramics. Ferroelectric ceramics do not possess any piezoelectric properties owing to the random orientations of the ferroelectric domains in the ceramics before poling. During poling, a DC electric field is applied on the ferroelectric ceramic sample to force the domains to be oriented or “poled”. While domains cannot be perfectly aligned with the field except when the grain or crystal is coincidentally oriented with its c- or a-axis in the field direction, their polarization vectors can be aligned to maximize the component resolved in the field direction. After poling, the electric field is removed and a remanent polarization and remanent strain are maintained in the sample, and the sample exhibits piezoelectricity. A simple illustration of the poling process is shown in Figure 1.2. But a very strong field could lead to the reversal of the polarization in the domain, known as domain switching.

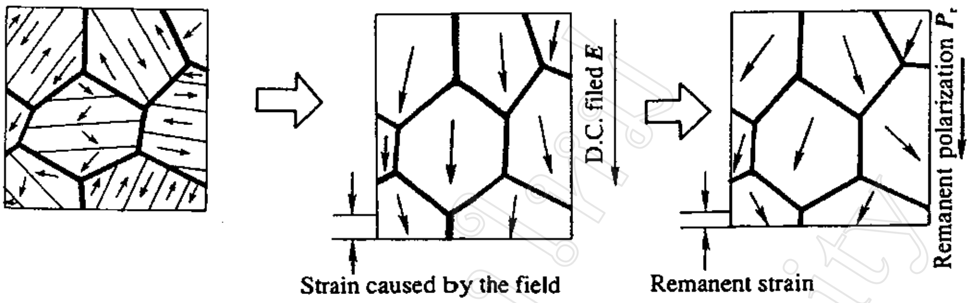
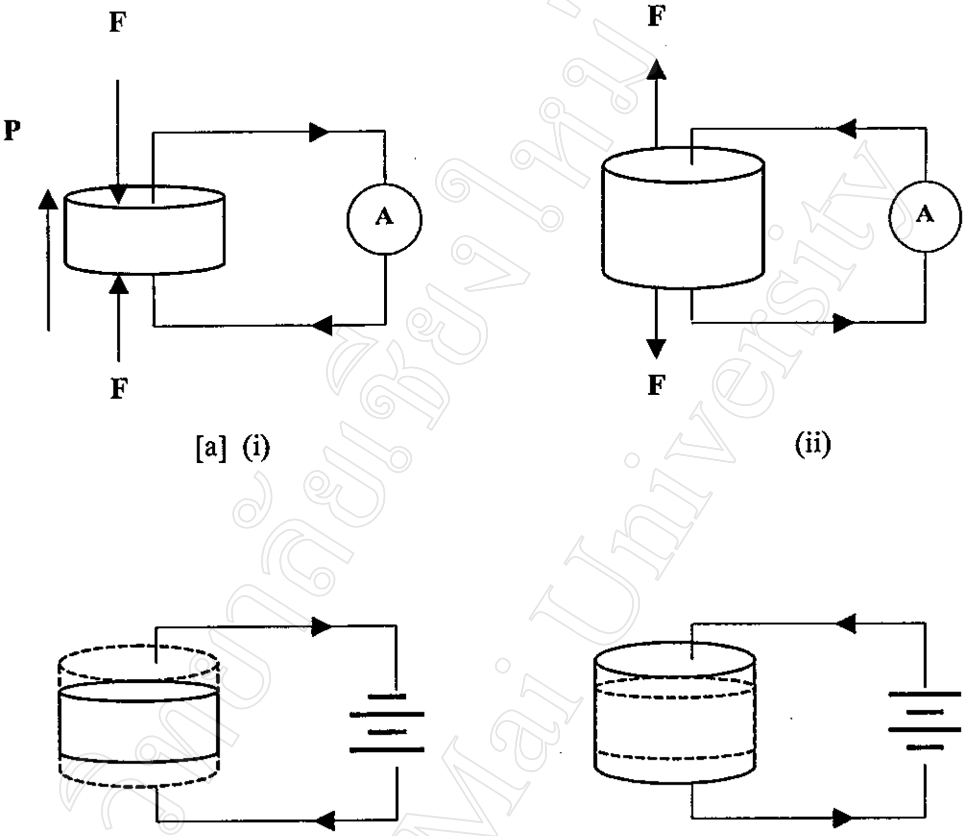


Figure 1.2 Schematic illustration of the poling process[18].

Two effects are operative in piezoelectric crystals and in ceramics are the direct effect (or a generator) and the converse effect (or a motor). The direct effect is identified with the electrical charge is generated from a mechanical stress, whereas the converse effect is associated with the mechanical movement generated by the application of an electrical field. Both effects are illustrated in Figure 1.3.

The piezoelectric coupling factor (e.g. k_{33}, k_{31} and k_p) is a convenient and direct measurement of overall strength of the electromechanical, i.e., the ability of ceramic transducer to convert one form of energy to another. It is defined as the square root of the ratio of energy output in electrical form to the total mechanical energy input (direct effect), or the square root of the ratio of the energy available in mechanical form to the total electrical energy input (converse effect). Because the conversion of the electrical to mechanical energy is always incomplete, k is always less than unity. The higher k values are most desirable and constantly sought after in new materials. For ceramics, k_p is a typical measurement used in comparing materials values ranging from 0.35 for $BaTiO_3$ to as high as 0.72 for PLZT.



[a] (i) (ii)

[b] (i) (ii)

Figure 1.3 [a] direct piezoelectric effect

[b] indirect piezoelectric effect

(i) contraction

(ii) expansion

where P is Polarization

F is Force

A is Current

The dash lines indicate the original dimensions[19].

The poling process is the critical element that can utilize the piezoelectric effect in a ferroelectric ceramics. Without poling, the ceramic is inactive even though each one of the individual crystallites is piezoelectric itself. With poling, the ceramic becomes extremely useful except it is heated above its Curie temperature (T_c) where it losses its polarization and all of the orientation of the polarization produced by the poling process[20].

1.2.2 Perovskite structure

Lead zirconate titanate (PZT) has the perovskite crystal structure with lead atoms occupied at the corner of the unit cell, the oxygen atoms situated at the surface centers while titanium (or zirconium) atoms located at the center of the unit cell, as shown in Figure 1.4.

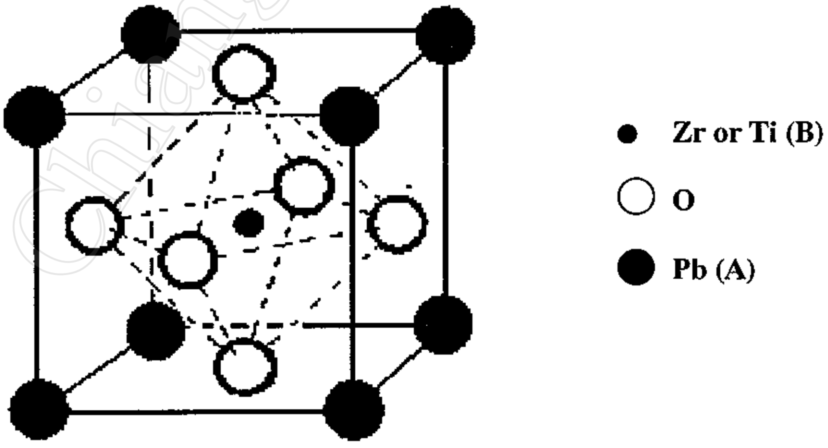


Figure 1.4 Basic structural unit of perovskite PZT[18].

Both the lead and oxygen ions have radii of about 0.14 nm. They make up a face-centered-cubic array, having a lattice parameter of nearly 0.4 nm. Octahedrally coordinated titanium or zirconium ions are located at the center of the unit cell. Sometimes the cubic is replaced by polyhedral. The O anions (e.g. oxygen) that surround each B cations (e.g. zirconium or titanium) are closely bound to it from the points of an octahedron and the basic structural unit becomes a group of eight corner-shared octahedrons around an A cation (e.g. lead). The bulk crystal is a continuous three-dimensional network of BO_6-octahedral groups (Figure 1.5)

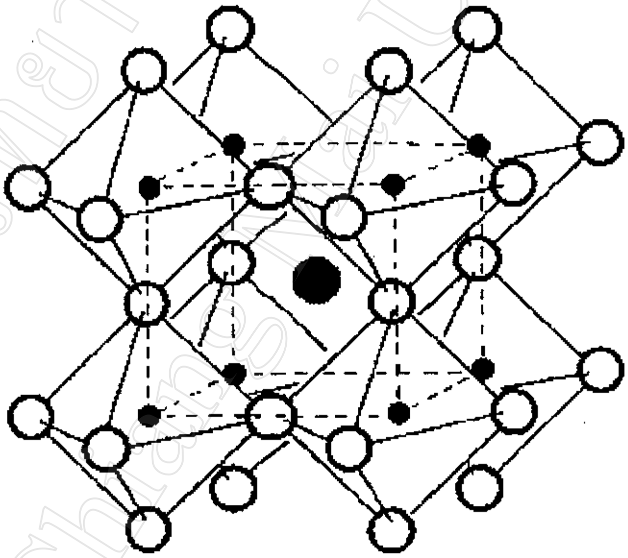


Figure 1.5 Octahedral framework with an A atom lie at the center of the unit cell[21].

Lead zirconate titanate (PZT) is a solid solution of the $PbZrO_3$-$PbTiO_3$ binary system. The chemical formula is $Pb(Zr_xTi_{1-x})O_3$ where $0<x<1.00$. Its phase diagram is shown in Figure 1.6. T_c line is the boundary between the cubic paraelectric and ferroelectric phase (PE-FE phase) side. At room temperature, the solid solution between lead titanate, $PbTiO_3$ (PT), and lead zirconate, $PbZrO_3$ (PZ), presents two ferroelectric phases, a tetragonal one in the titanium rich side and a rhombohedral one in zirconium rich side. Dielectric and piezoelectric maximum properties can be found in the ceramics at the composition near $Pb(Zr_{0.52}Ti_{0.48})O_3$ which corresponds to the tetragonal-rhombohedral phase transition composition as see in Figure 1.7[22]. This transition is usually classified as morphotropic because it corresponds to a structural change with the variation in composition. The important properties observed in PZT materials near this phase transition justify the large interest devoted to this region of the phase diagram. Although a line in the phase diagram represents this transition, it is commonly to observe that the tetragonal and rhombohedral phases may coexist in a finite range of compositions around the morphotropic phase boundary (MPB) in ceramics.

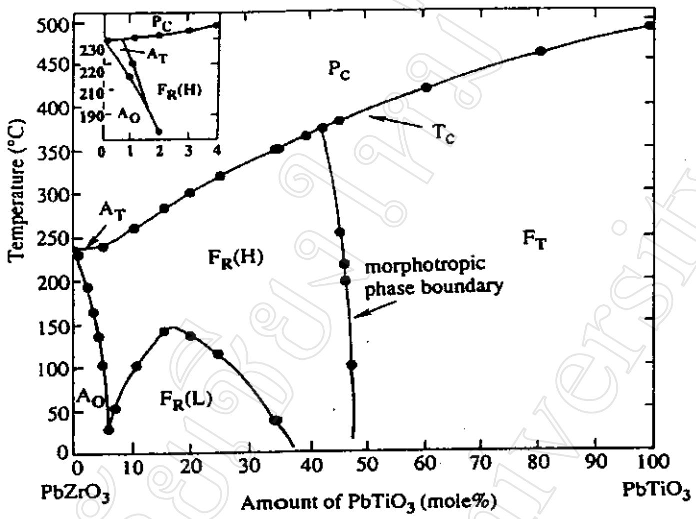


Figure 1.6 Phase diagram of the $PbTiO_3$-$PbZrO_3$ solid solution[22].

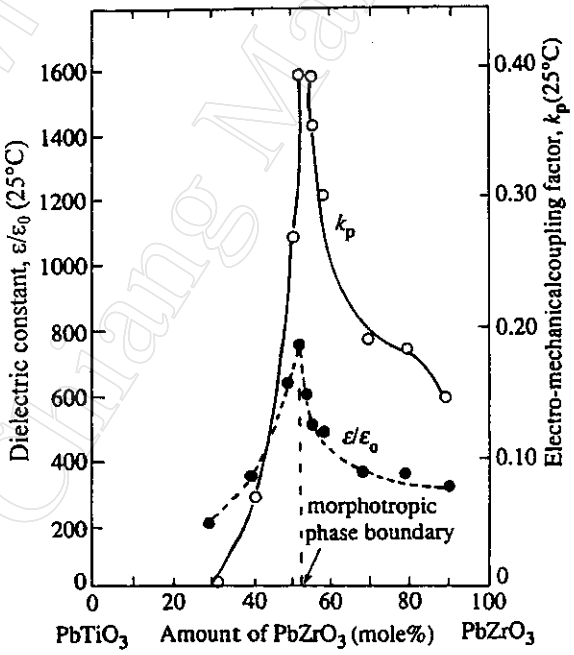


Figure 1.7 Dielectric and piezoelectric properties of the $PbTiO_3$-$PbZrO_3$ solid solution[22].

At room temperature, this boundary is at the ratio of Zr:Ti = 52:48. The lattice parameters of the PZT also change near the composition corresponding to the MPB (as see in Figure 1.8). In the region where Zr/Ti lies between 100/0 and 94/6, the solid solution is an antiferroelectric, orthorhombic phase exhibiting no observerable piezoelectric effect[23].

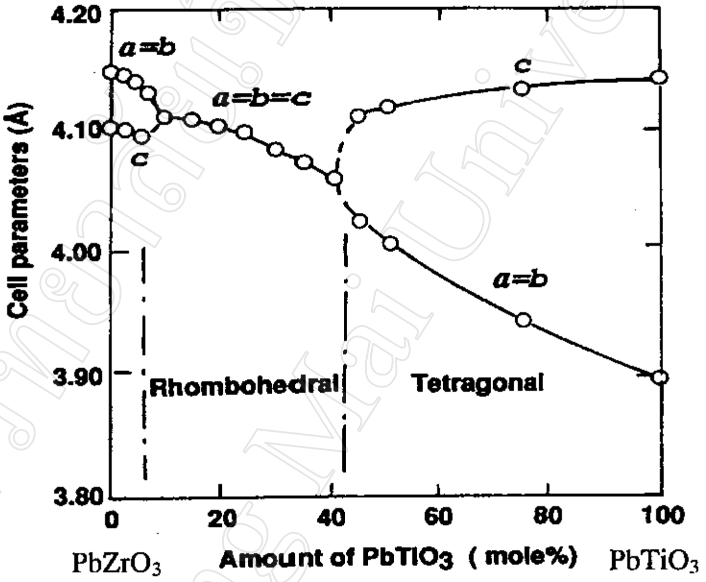


Figure 1.8 Lattice parameter change at room temperature for the PbTiO$_3$-PbZrO$_3$ solid solution[23].

Figure 1.9 showed the structure changes at the Curie temperature (T_c) and the morphotropic phase boundary. Titanium-rich compositions in the PZT system favor a tetragonal modification with sizeable elongation along [001] and a large spontaneous polarization in the same direction. There are six equivalent polar axes in the tetragonal phase corresponding to [100], $[\bar{1}00]$, [010], $[0\bar{1}0]$, [001], and $[00\bar{1}]$ directions of the cubic paraelectric state. A rhombohedral ferroelectric state is favored for zirconium-rich compositions. Here the distortion and polarization are along [111] directions, giving rise to eight possible domain states: $[111]$, $[\bar{1}11]$, $[1\bar{1}1]$, $[11\bar{1}]$, $[1\bar{1}\bar{1}]$, $[\bar{1}\bar{1}1]$, $[\bar{1}1\bar{1}]$, and $[\bar{1}\bar{1}\bar{1}]$. There are fourteen possible poling directions near the MPB over a very wide temperature range, which may in part explain the ceramic piezoelectric behavior near this boundary[24].

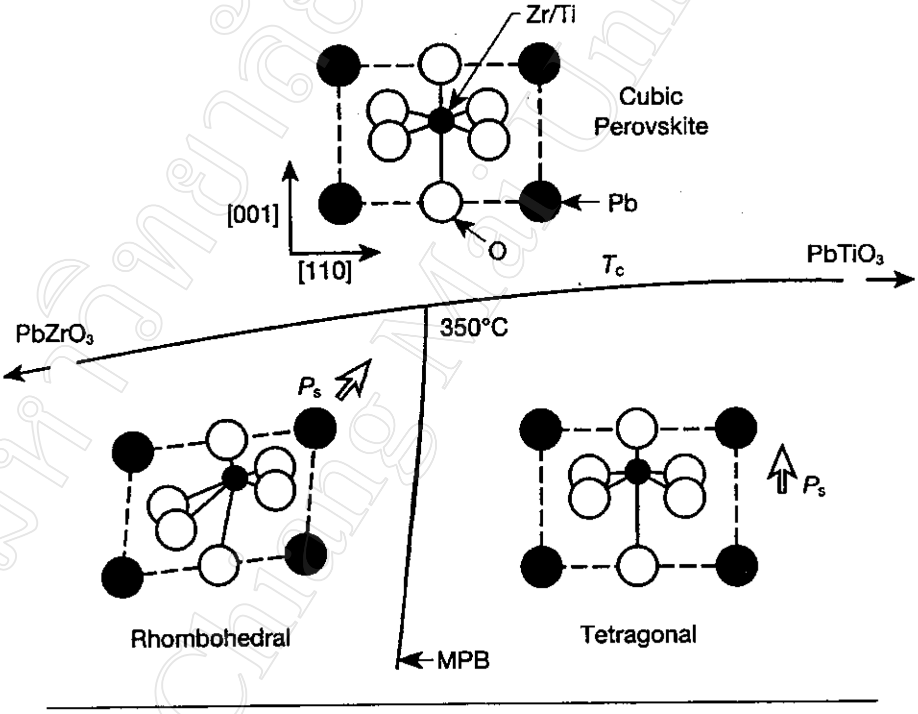
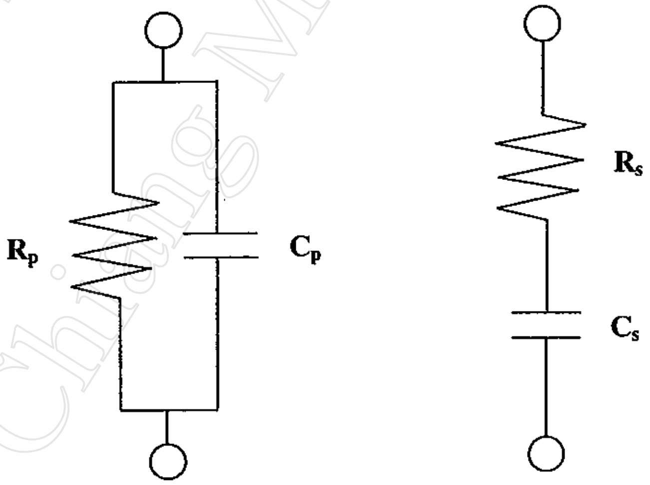


Figure 1.9 A portion of the PbTiO$_3$-PbZrO$_3$ phase diagram[24].

1.2.3 Dielectric constant of PZT

The dielectric constant, or relative permittivity (ε_r) is defined as the ratio of the permittivity of the material to the permittivity of free space. The dielectric loss factor is defined as the tangent of the loss angle (tan δ). The loss factor represents the ratio of resistance of a parallel equivalent circuit of the ceramic element (Figure 1.10). It is a measure of the amount of electrical energy which is lost through conduction when a voltage is applied across the piezoelectric element. The dielectric constant (ε_r) and dielectric loss factor (tan δ) can be measured using a standard impedance bridge or an impedance analyzer both of which provide a direct reading. Measurements are generally carried out at 1 kHz to measure the static parameters, away from mechanical resonance, at a low applied electrical field[25].



(a) Parallel (b) Series

Figure 1.10 Equivalent circuit of a piezoelectric element (non-resonance operation)[25].

1.3 MODIFIED PZT

PZT ceramics are always used with a modifier to improve or optimize their basic properties for specific applications. Though the maximum piezoelectric effect was found in a composition of pure PZT at the MPB, but in practice, Modified PZT ceramics are often used for various applications. For examples, for materials use as an underwater sound projector, a small dielectric loss ($\tan\delta$) and a high sharpness of the resonance frequency (Q_m) under high fields are desirable, while for materials used for acoustic transformer, a high electromechanical coupling coefficient (K_p) and a high relative permittivity (ε_r) are required. Basically, three type of additives have been employed in the compositional modification of PZT. These typical additives and their effects on the piezoelectric properties of PZT are shown in Table 1.1

The first additives used in compositional modification of PZT are off-valent donors (soft dopants), such as, Nb^{5+} replacing Zr^{4+} or La^{3+} replacing Pb^{2+}, to counteract the natural p-type conductivity of the PZT and increase the electrical resistivity of the materials by at least 3 orders of magnitude. The donors are usually compensated by A-site vacancies. These additives enhance domain reorientation. Ceramics produced with these additives are characterized by square hysteresis loops, low coercive fields, high remanent polarization, high dielectric constants, maximum coupling factors, higher dielectric loss, high mechanical compliance, and reduced aging.

Table 1.1 Typical additives for PZT and their major effects on piezoelectric properties[26].

Additives				Major Effects
Type	Replaced site	Atom	Ionic radii	
Soft-dopants (off-valent donors)	Pb^{2+}	La^{3+}	0.122	Higher permittivity Higher K_p Much lower Q_m Resistivity about 10^3 higher
		Nd^{3+}	0.155	
		Sb^{3+}	0.090	
		Bi^{3+}	0.114	
		Th^{4+}	0.110	
	Ti^{4+} or Zr^{4+}	Nb^{5+}	0.069	
		Ta^{5+}	0.068	
		Sb^{5+}	0.063	
		W^{6+}	0.065	
Isovalent	Pb^{2+}	Ba^{2+}	0.134	Lower Curie point Higher permittivity
		Sr^{2+}	0.112	
	Ti^{4+} or Zr^{4+}	Sn^{4+}	0.071	
Hard dopants (off-valent acceptors)	Pb^{2+}	K^{+}	0.133	Lower permittivity Lower K_p Much higher Q_m Lower dielectric loss
		Na^{+}	0.094	
	Ti^{4+} or Zr^{4+}	F^{3+}	0.067	
		Al^{3+}	0.057	
		Sc^{3+}	0.083	
		In^{3+}	0.092	
		Cr^{3+}	0.064	

Isovalent additives, such as Ba^{2+} or Sr^{2+} replacing Pb^{2+} or Sn^{4+} replacing Zr^{4+} or Ti^{4+}, in which the substituting ion is of the same valency and approximately the same size as the replaced ion. These additives usually inhibited domain reorientation and poorly developed hysteresis loops. Other properties include lower dielectric loss, low compliance, and higher aging rates.

Off-valent acceptors, such as Fe^{3+} replacing Zr^{4+} or Ti^{4+}, are compensated by oxygen vacancies and usually have only limited solubility in the lattice. Domain reorientation is limited. The ceramics with acceptor additives are characterized by poorly developed hysteresis loops, lower dielectric constants, low dielectric losses, low compliances, and higher aging rates.

Dopants are usually added in concentrations of ≤ 3 mole %. Modifiers are substituted into the original PZT composition as solid-solution constituents in concentrations of ≥ 5 at. %. The most common examples of modifier systems are $(Pb,La)(Zr,Ti)O_3$, $(Pb,Sr)(Zr,Ti)O_3$, $(Pb,Ba)(Zr,Ti)O_3$, $Pb(Zr,Ti,Sn)O_3$, $(Pb,La)TiO_3$ and $Pb(Mg,Nb)O_3$-$PbZrO_3$-$PbTiO_3$. There are many of the lead containing, solid-solution systems[22]. But one system that embraces all compositional aspects of the dielectric, piezoelectric, pyroelectric, ferroelectric, and electrooptic ceramics is the PLZT system[27].

1.3.1 Phase diagram of the PZT-PLZT solid-solution system

Modification of the PZT system by addition of lanthanum has a beneficial effect on several of the basic properties of the material. The PLZT phase diagram[19] is shown in Figure 1.11.

when y is the percentage of the occupied La sites, and
z is the percentage of the Zr atoms

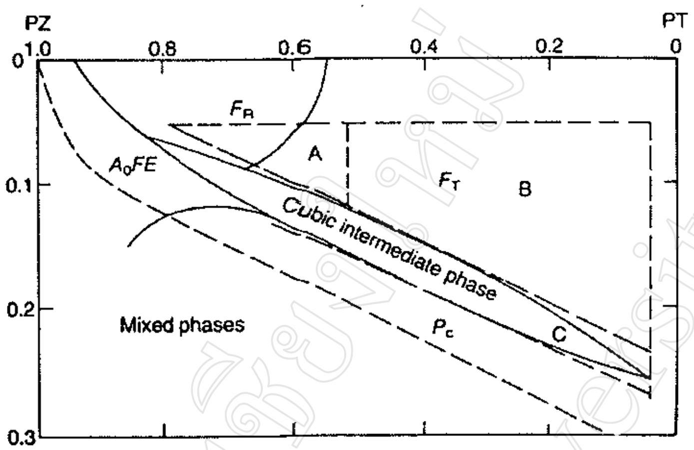


Figure 1.11 Phase diagram of $Pb_{1-3y/2}La_y(Ti_{1-z}Zr_z)O_3$; (A) memory, (B) linear, (C) quadratic[19].

And in Figure 1.12, shows the PLZT system with the parent PZT phase diagram. Several areas on the diagram are explained.

(1) the ferroelectric tetragonal and rhombohedral phases are shown in FE_{tet} and FE_{rhom}.

(2) the orthorhombic antiferroelectric phases is AFE_{ortho}.

(3) the cubic paraelectric (paraelectric, nonferroelectric) phases in PE_{cubic}.

(4) the morphotropic phase boundary (MPB) in magneta.

(5) the pyroelectric application areas near $PbTiO_3$ in ●

(6) the economically important MPB compositions that embrace almost all of the transducer applications in mixed phase area.

(7) specific compositions in these regions in ▨

The figure shows the effect of adding lanthanum to the PZT system is decreasing the stability of the ferroelectric phases in favor of the paraelectric and antiferroelectric phases which shows the reduction of the T_c with increasing lanthanum. At a 65/35 ratio of PZ/PT, a concentration of 9.0% lanthanum (designated as 9/65/35) is sufficient to reduce the temperature of the stable ferroelectric polarization by slightly below room temperature, resulting in a material that is nonferroelectric and cubic in its virgin state. The crosshatched area existing along the ferroelectric-paraelectric phase boundary denotes a region of diffuse, metastable relaxor phases that can be electrically induced to a ferroelectric phase. Materials within this region exhibit a quadratic strain and electrooptic behavior.

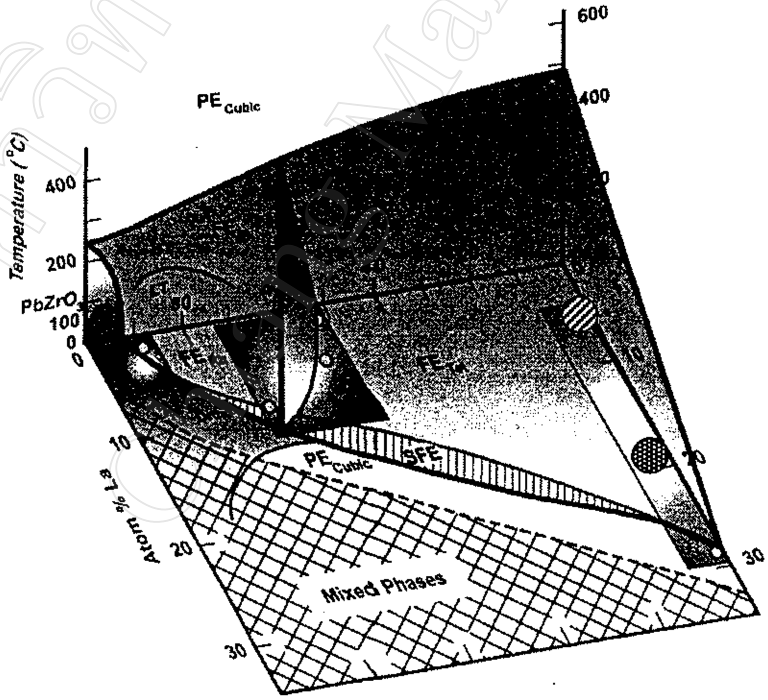


Figure 1.12 Phase diagram of $Pb_{1-3y/2}La_y(Ti_{1-z}Zr_z)O_3$[17].

The solubility of lanthanum in the PZT lattice is a function of composition and is related directly to the amount of PT present. The compositional dependence of the solubility limit is indicated by the dashed line adjacent to the mix-phase region (double crosshatched area). For the two end-member compositions, PZ and PT, these limits are 4 and 32 mole %, respectively. The solubility limits for intermediate compositions are proportional to their Zr/Ti ratio.

In this thesis, the amounts of La atoms in PZT are 8, 9, 10 and 12 mole %La atoms at a 65/35 ratio of PZ/PT.

1.4 POWDER PROCESSING ROUTE

Most ceramics are made by the powder-processing route. Ceramics powders are crucial to the subsequent processing as well as the properties of final ceramics. The desirable characteristic of ceramic powders include not only high degree of chemical purity, controlled chemical and phase homogeneity, but also a fine particle size to promote sintering, a narrow particle size distribution to inhibit grain growth and dispersability to remove defects.

1.4.1 Solid-State Reaction

The most direct method of making mixed-oxide is to react a mixture of metal oxides, hydroxides or salts in the solid state. Conventional processing to prepare multicomponent mixed-oxide ceramic powders involves three steps of mixing, solid-state reaction and milling. The multicomponent phases are formed via solid-state reactions. Consequently, these solid-state reactions typically result in the formation of aggregates (hard agglomerations) that require a moderate process to reduce the particle size to the micrometer level. But milling to particle size below 1 μm is technically difficult for some hard materials[28], contaminates the product and is energy intensive[29]. The homogeneity and purity of the powder are poor whereas the particle size distribution is broad. The need to calcine the starting mixture at a high temperature raises the costs and agglomeration, and in some cases, e.g. during PZT synthesis, results in loss of volatile oxides such as lead oxide. Despite the disadvantages mentioned above, this conventional process has still been widely used in industry for producing PZT powders due to its simplicity and low cost. Furthermore, since PZT is a relatively soft material, milling with one of its component zirconia media will not cause a significant problem of contamination. Especially with the advancement of high-energy milling technology, submicron-sized PZT powder with narrow particle size distribution and improved chemical homogeneity has been fabricated recently[30].

1.4.1.1 One-stage solid-state reaction process

Conventionally, PZT powders are prepared by one-stage solid-state reactions in a mixture of PbO, ZrO_2 and TiO_2 powders. According to Mastsuo & Sasaki[31], there are four regions corresponding to four chemical processes during calcination (see Figure 1.13),

region I: no reaction ($T<350°C$);

region II: $PbO + TiO_2 \rightarrow PbTiO_3$ ($350°C < T < 700°C$);

region III: $PbTiO_3 + PbO + ZrO_2 \rightarrow Pb(Zr_{1-x}Ti_x)O_3$ ($650°C<T<800°C$);

region IV: $Pb(Zr_{1-x}Ti_x)O_3 + PbTiO_3 \rightarrow Pb(Zr_{1-x'}Ti_{x'})O_3$ ($x<x'$) ($800°C<T<1000°C$).

In industrial production, calcining procedure normally involves maintaining the product temperature at 650 °C for 1 ~ 2 hours and then at about 850 °C for 2 hours[20].

As shown in Figure 1.13, the reaction mechanism of the conventional one-stage solid-state reaction leading to PZT solid-solution formation actually involves in several steps, with $PbTiO_3$ (PT) formation at an early stage of the reaction followed by some intermediate phases formation[32, 33].

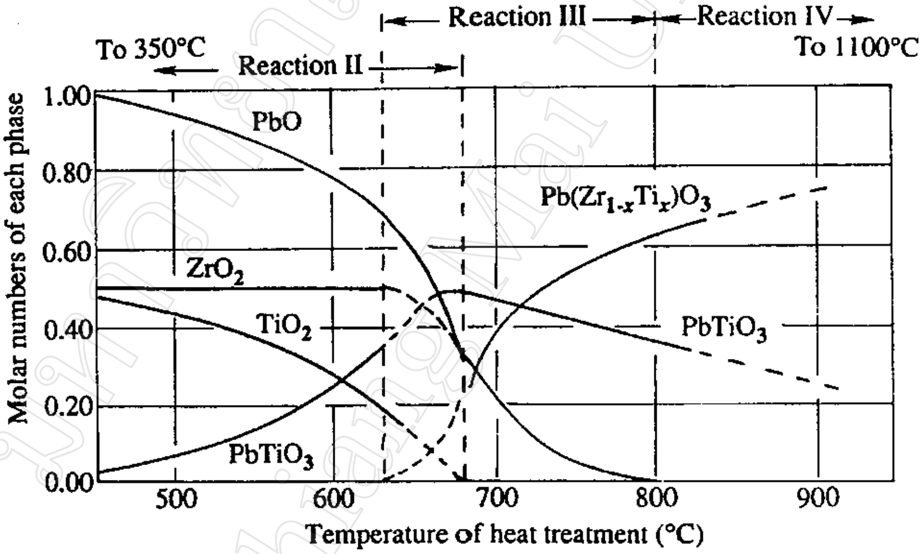


Figure 1.13 Four regions of solid-state reaction appear as the calcination temperature increases[31].

The conversion of the intermediate phases into PZT involves long-range diffusion resulting in compositional fluctuation[34]. Atomic-level uniform distribution of Zr/Ti ions at the B site of the ABO_3 perovskite structure cannot be ensured, and the completion of the reaction by long-range diffusion also requires higher temperature (>800°C) calcination which will exceed the volatilization temperature of PbO. However, Kakegawa *et al.*[35] reported that the compositional fluctuation arises mainly at the site of Zr^{4+} and Ti^{4+} in the PZT system and that the stoichiometry can be easily attained between an A-site ion and a B-site ion in the perovskite type compound of ABO_3 [36]. Therefore, an improved two-stage solid-state reaction process has been proposed.

1.4.1.2 Two-stage solid-state reaction process

In this process, $(Zr_{1-x}Ti_x)O_3$ powder (ZTO) is synthesized as the first step, followed by solid-state reaction between ZTO and PbO powder, which eliminates intermediate phases while going directly to the PZT perovskite phase. The simplified reaction consequences of the two-stage process can be illustrated as follows:

stage I: $(1-x)\ ZrO_2 + x\ TiO_2 \rightarrow Zr_{1-x}Ti_x\ O_4$

stage II: $Zr_{1-x}Ti_x\ O_4 + PbO \rightarrow PZT$.

The ZTO powder can be prepared either by conventional solid-state reaction route[4, 37] or by chemical synthesis routes, such as coprecipitation[38], spray -pyrolysis[35], melt salt synthesis[39], and hydrothermal process[40, 41]. By using this two-stage process, compositionally homogeneous PZT powders can be synthesized at lower calcination temperatures (600 °C) and in shorter calcination duration. The resulting PZT powders are more sinterable due to the reactive calcination[42] and have fine particle size because the associated morphological development results in a sponge, skeletal-type structure consisting of ultrafine particulates that can be readily broken down further by milling (see Figure 1.14). The highly reactive powders allow densification at temperatures 100 to 200 °C lower than that reported for conventionally one-stage process[4, 43].

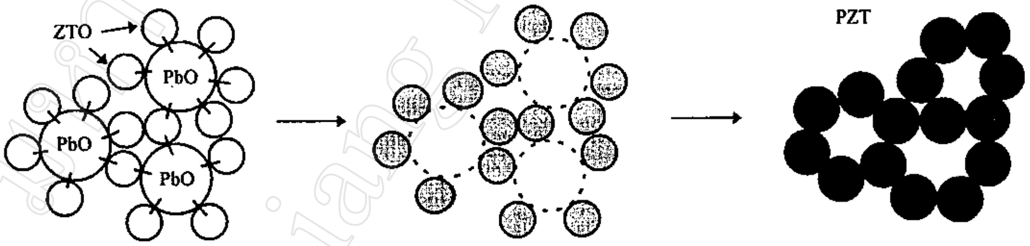


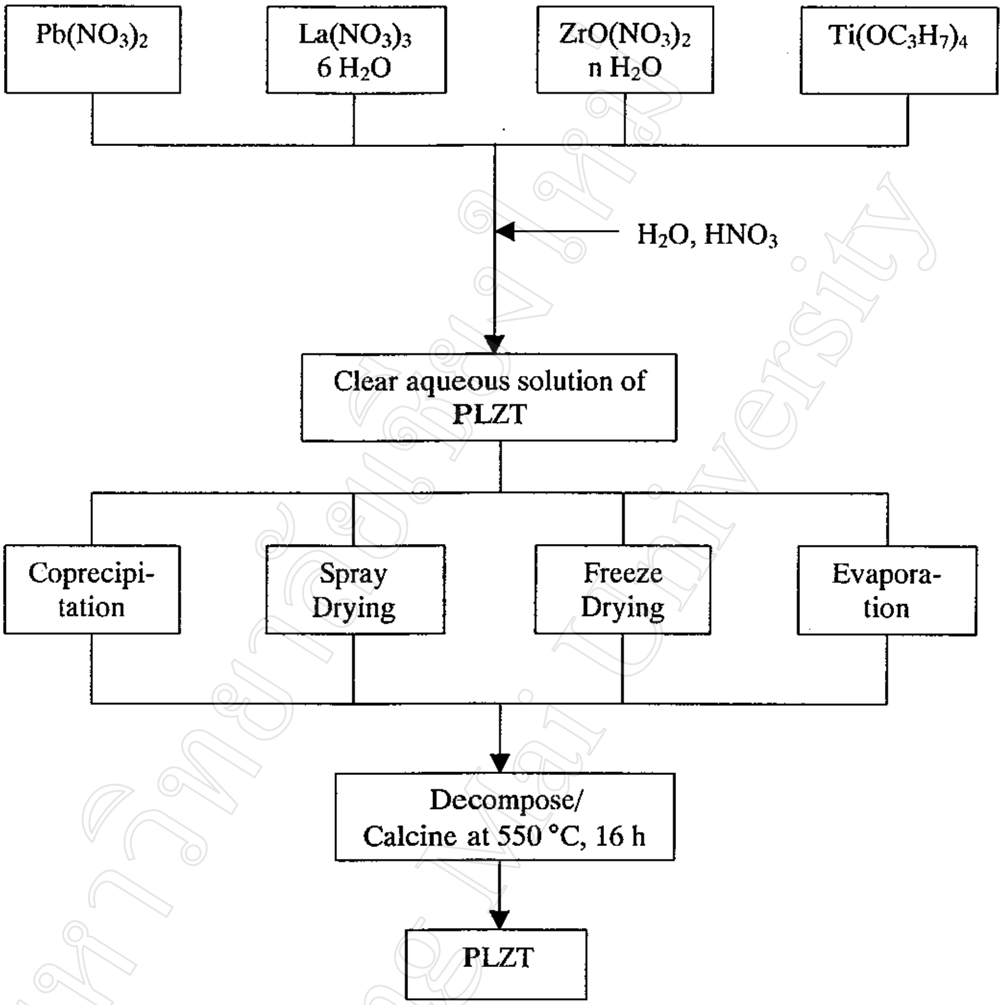
Figure 1.14 Schematic representation of the perovskite PZT powder formation process via two-stage solid-state reaction and associated morphological change[4].

1.4.2 Chemical Synthesis

Chemical synthesis of mixed-oxide powders in principle can promote the chemical homogeneity, purity and lower processing temperatures because of mixing of the starting materials in the solution state and the fine particles produced[44]. The chemical synthesis methods have been used to make PZT powders are coprecipitation, sol-gel, melt salt, spray pyrolysis and hydrothermal syntheses.

1.4.2.1 Coprecipitation from solution

Coprecipitation from solution is the wet chemical techniques for the preparation of mixed oxides. It consists of preparation of an aqueous solution which contains the precipitating agent. The precipitated product is separated from the liquid by filtration, dried and thermally decomposed to the desired compound. Several parameters, such as pH, mixing rates, temperature and concentration have to be controlled to produce satisfactory results. The composition control, purity and morphology of the resulting products are managable. However, different rates of precipitation of each individual compound may lead to microscopic inhomogeneity, and agglomerates are generally formed during calcination, as with other solution techniques. By controlling the synthesis conditions, this method can produce stoichiometric electroceramic powders of high purity and fine particle size at a relatively moderate cost and is currently applied widely to make electroceramic powders in industry[45]. It has been reported for making PZT powders in combination with spray and freeze drying techniques since 1960's[15, 46- 49] as shown in Figure 1.15. Spray drying is a technique which consists of a rapid vaporization of the solvent contained in small droplets of the required solutions of cations, whereas freeze drying utilizes slow sublimation of the solvent. These techniques afford excellent control over impurity levels and compositions, and generate homogeneous fine particles. Utilizing rapid vaporization or slow sublimation of the solvent, they reduce the agglomeration problem associated with the large surface tension of vapor-liquid interface. PZT powders of adequate purity, homogeneity and stoichiometry have been made[50]. The PZT powders are spherical with high surface area, but the spray dried particles are relatively large (about 2 to 3 μm) and need to be calcined under a controlled atmosphere[51]. Wang *et al.*[6] reported another modified coprecipitation process by thermally decomposing metal-EDTA complexes derived from nitrate salt solutions to prepare PZT powder at a low temperature. A similar process was reported by Potdar *et al.*[52], in which the reactions of sodium zirconyl oxalate, potassium titanyl oxalate and lead nitrate in their stoichiometric ratios at room temperature precipitate a molecular precursor lead zirconyl titanyl oxalate (PZTO). The controlled pyrolysis of PZTO at 500°C for 6 h in air resulted in crystalline submicron-sized PZT powders. Recently, a theoretical approach by considering the thermodynamic equilibrium constants, the solubility and ionic equilibria relationships for individual metal hydroxides in aqueous media has also been reported to optimize the pH for the coprecipitation of the ternary Pb-Zr-Ti system[53].



Figue 1.15 Flow diagram for preparing PLZT nitrate solutions[15].

1.4.2.2 Molten salt synthesis

This process is based on the use of a molten salt solvent instead of water in coprecipitation to act as the medium of reaction between the constituent oxides. The desired compound will form if it is thermodynamically more stable than the constituent oxides and this stability is based on more than simple entropy of mixing. The product's greater stability translates into its having a smaller molten salt solubility than any of the constituent oxides. However, because of the small diffusion distances in an intimate mix of the constituent oxides in the molten salt, complete reaction is accomplished in a relatively short time. The reaction proceeds by supersaturation of the molten salt solvent by the constituent oxides with respect to the product compound, which precipitates from the solution. This synthesis process has been used to make PZT powders by using NaCl-KCl as solvent at 1000 °C for 1 h, but a small amount of ZrO_2 residue was found due to the incomplete reaction[54]. However, since morphology control of electroceramic powders is possible by this process[55], it has been used to prepare needle-like PZT powders[39].

1.4.2.3 Spray pyrolysis

Spray pyrolysis differs from spray drying in the use of solutions, the consequent process of precipitation or condensation within a droplet, and the use of significantly higher temperatures (>300 °C) to form the desired inorganic phase by pyrolysis[11]. During spray pyrolysis, the solution is atomized into a series of reactors where the aerosol droplets undergo evaporation and solute condensation within the droplet, drying, thermolysis of the precipitate particle at higher temperature to form microporous particles and, finally, sintering of the microporous particles to form a dense particle. This process integrates the precipitation, calcination and sintering stages of powder synthesis into a single continuous process which afford good control of the morphology of the powders. This solution aerosol technique takes advantage of many of the available solution chemistries that have been developed for powder synthesis and also uniquely controls the particle formation environment by compartmentalizing the solution into droplets. In this manner, spray pyrolysis ensures complete stoichiometry retention on the droplet scale, and has been used to prepare submicron-sized spherical PZT powders[56]. However, the pyrolysis temperature for PZT formation is about 900°C, while minor $PbTiO_3$ phase was found in the PZT powders when pyrolysis temperature was lower.

1.4.2.4 Sol-gel

The sol-gel processing consists of the formation of an amorphous gel from solutions followed by dehydration at relatively low temperature and pressure. Since it starts from a solution of all components in the form of soluble precursor compounds, the mixing at a molecular level is retained through gel formation. The most advantageous characteristics of this method are the high purity and excellent control of the composition of the resulting powders. Metal alkoxides or salts are partially hydrolyzed which leads to branching and crosslinking. This polymerization reaction forms three dimensional structures and avoids any segregation phenomena. Then the rigid coherent gel is dried and heated at temperatures lower than with other techniques, the overall sol-gel process is schematically shown in Figure 1.16[57]. The sol-gel method can produce high quality fine electroceramic powders with excellent homogeneity but the process is expensive because of the raw materials used and the need to calcine the amorphous powder at high temperature to obtain the desired crystallinity. Furthermore, large shrinkages will normally occur during processing. Therefore, this technique is not suitable for bulk component fabrication, but applicable for films. Though there were some early reports demonstrating the preparation of PZT powders either by alkoxide[58, 59] or by non-alkoxide sol-gel methods[60, 61], this method is not as successful in making PZT powders as in making PZT thin films.

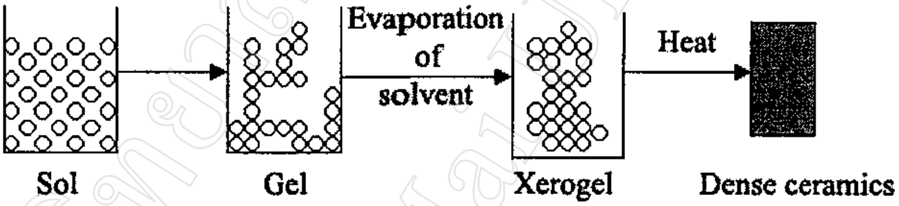


Figure 1.16 The overall sol-gel process[57].

However, it is difficult to get phase-pure perovskite PZT powders at low temperatures. Either pyrochlore $Pb_2(Ti/Zr)_2O_6$ phase or Pb and PbO phases have been observed during precursor pyrolysis depending on precursor types and synthesis conditions[62]. Because of the nature of sol-gel process, the synthesis is started from metal-organic precursors in organic solvents, and controlling the carbonaceous content of the precursor. The rate of hydrocarbon release during pyrolysis is critical to avoid the formation of unwanted phases[63]. This effect is certainly easier to control in relatively small dimensional thin films than that in relatively large dimensional powders.

1.4.2.5 Emulsion synthesis

This process is generally applicable for many ceramic powders or combinations of ceramic powders for which water-soluble precursors are available[64].

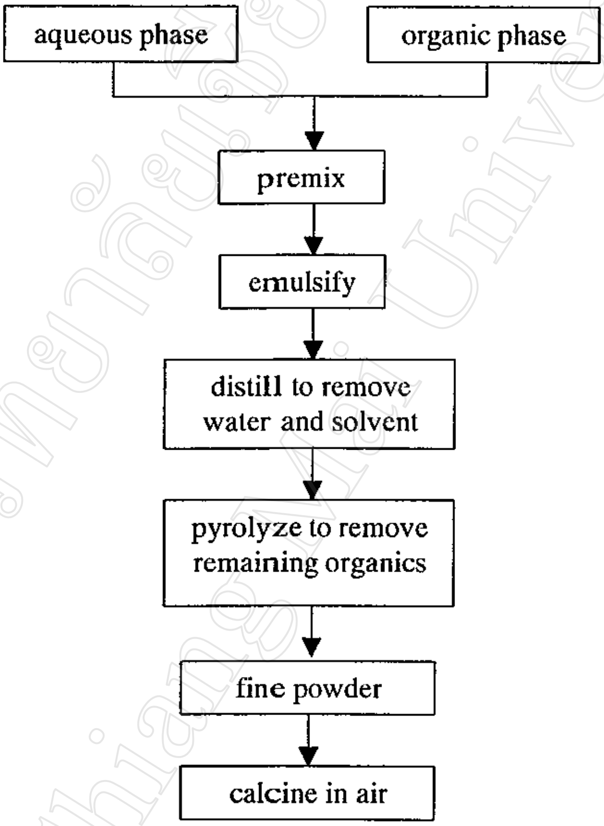


Figure 1.17 Flow chart of emulsion process[64].

From Figure 1.17, the aqueous solution of the ceramic precursors is emulsified with an organic fluid containing an organic surfactant to provide a dispersion of aqueous droplets of nearly uniform size in the organic fluid. Since the original aqueous solution is homogeneous and the dispersed water droplets in the organic phase are uniform in size, each water droplet contains essentially the same amount of ceramic material.

The emulsion process uses water-soluble precursors dispersed in the organic phase to produce spherical, uniform fine powders with minimized agglomeration at a relatively moderate cost. However, few studies have been reported for making PZT powders by this process[65], probably because it encounters similar problems to those in sol-gel processing.

1.4.2.6 Hydrothermal synthesis

Hydrothermal synthesis can be defined as the treatment of aqueous solutions or suspension of precursors at elevated temperature in pressurized vessels[66]. It is an aqueous chemical route for preparation of crystalline, anhydrous ceramic powders and can be easily differentiated from other process, such as the sol-gel and coprecipitation processes, by the temperatures and pressures used in the synthesis reactions as seen in Figure 1.18. Typically, temperatures range from the boiling point of water to the critical temperature of 374°C and pressures range up to 15 MPa. The specific conditions employed should be capable of maintaining a solution phase that provides a labile mass transport path promoting rapid phase transformation kinetics. The combined effect of pressure and temperature can also reduce free energies for various equilibria-stabilizing phases that might not be stable at atmospheric conditions[67]. The basic mechanism for the hydrothermal formation of ceramic oxide particles is described as a dissolution/precipitation and/or *in-situ* transformation process. The dissolution/precipitation mechanism is operative when the suspended reactant particles, normally oxides, hydroxides, of component oxides, can dissolve into solution, supersaturate the solution phase, and eventually precipitate out product particles. The driving force in these reactions is the difference in solubility between the oxide phase and the least soluble precursor or intermediate.

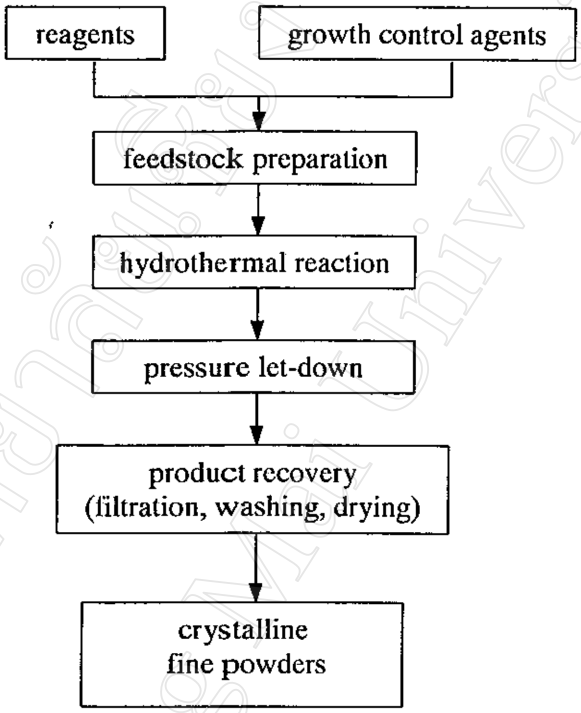


Figure 1.18 Flow chart of hydrothermal synthesis[75].

In many cases, the suspended solids are not soluble enough in aqueous solution, and hence, either mineralizers such as bases have to be added, or ceramic particles are formed via another in-situ transformation mechanism in which the suspended particles undergo a polymorphic or chemical phase transformation[68].

In some cases, both mechanisms might be in operation depending on the synthesis conditions[69,70]. The hydrothermal synthesis of ceramic powders possesses two major advantages: the elimination or minimization of any high temperature calcination stage and the use of relatively inexpensive raw materials. Specifically, this process is limited to oxides which can be formed under hydrothermal conditions. Thus, it is particularly suitable for preparing electroceramic powders such as PZT.

The advantages of hydrothermal are summarized as follows;[71]

(1) The process utilizes comparatively inexpensive precursor chemicals such as oxides, hydroxides, chlorides, acetates and nitrates rather than alkoxides.

(2) Reactants, which are normally volatile at the required reaction temperatures, tend to condense during the hydrothermal process maintaining the reaction stoichiometry, and so high-purity multi-component ferroelectric powders can be obtained.

(3) It is a low temperature process, with many effects achievable even below 300 °C. The relatively low temperature can break down stable precursors under pressure, which avoids the extensive agglomerations that the solid-state reaction usually cause at high temperature.

(4) The process is able to produce solid-solution particles with a controlled particle size distribution, morphology and complex chemical compositions; multi-doped perovskite ABO_3 ceramic powders, can be grown to submicrometer or even nanometer size by control of the nucleation and growth processes.

(5) Presintering or calcination stages are not needed in powders synthesized by the hydrothermal process. This feature is particularly important for synthesizing high-quality and reliable PZT powders because PbO is appreciably volatile (above

about 800°C) and hence even more so at the temperatures necessary for conventional calcination and sintering.

(6) The synthesis is accomplished in a closed system from which different chemicals can be recovered and recycled. That makes it an environmentally benign process.

(7) The process is able to do in the industrial scale. Potentially, hydrothermal synthesis gives the opportunity for cost-effective and reproducible manufacture of high-quality PZT powders on a large industrial scale.

The disadvantages of this process are;

(1) The moderately high initial cost of the apparatus.
(2) Safety issues related to high pressure processing.
(3) Potential high temperature corrosion problems arising from the presence of basic or acidic mineralizers.

The most commonly used precursors for the hydrothermal synthesis of PZT powders are nitrates, chlorides, oxychlorides, acetates, hydroxides and Zr or Ti alkoxides. The composition ratio of Ti/Zr is generally around 0.48/0.52 so that the desired composition $Pb(Ti_{0.48}Zr_{0.52})O_3$ is close to the morphotropic phase boundary zone in the phase diagram of $Pb(Ti_{1-x}Zr_x)O_3$ solid solution. Owing to the amphoteric nature of PbO, some PbO will remain in the solution after hydrothermal reaction. Ichihara *et al.*[72] reported that the addition of about 22% excess of a lead compound was necessary to obtain stoichiometric PZT powders. Excess lead has also been used to compensate for the evaporation loss occurring during subsequent sintering resulting in better electrical properties[73] and to produce a lower agglomeration state[74].

Catalyst or mineralizer is necessary for synthesized PZT powders because it increases the solubility of the starting precursors. The use of strong alkalis such as KOH or NaOH and halides such as KF, LiF, NaF, or KBr has been reported[75], which can lead to the formation of PZT under hydrothermal conditions. However, it was noted that lithium and fluorine, in combination or separately, were selectively retained as impurities in PZT, and that they also increased the level of retention of the associated alkali or halide[75]. The concentration of catalyst has strong influence on PZT formation. During the initial stage of PZT formation, $PbTiO_3$ and $PbZrO_3$ were produced at lower KOH concentrations (< 2 M), and PZT was produced at higher KOH concentrations (> 4 M) and formed very quickly in 10 M KOH solution[76]. Since the individual Pb, Ti, and Zr ion species have different solubility behaviors with increasing alkalinity of the solution, the formation mechanism of PZT from hydroxides is not very clear at the moment. The type of bases also plays an important role in the PZT powder characteristics. For example, the morphology of the PZT powder was cubic when KOH was used as catalyst, while the morphology tended to be tabular and the agglomerate size increased when NaOH was used[74].

Another important factor which influences the hydrothermal formation of PZT powder is temperature. Temperature and mineralizer have a combined effect on PZT formation. Experiments have shown that the rate of nucleation of PZT powder decreased with increasing temperature but that sufficient crystal growth occurs at temperatures as low as 150°C[77]. Crystalline PZT powder was not formed when the temperature was below 140 °C in the presence of 4 M KOH as a catalyst; the product was composed of huge PZT particles and gels[78]. PZT can be detected by X-ray diffraction when hydrothermally synthesized for 0.5 hour at 200 °C, 1 hour at 150 °C, 5 hours at 100 °C or 4 days at 70 °C in the presence of 10 M KOH as a catalyst. The particle sizes changed dramatically (from 1 μm to 5 μm) with the increase of temperature[76]. At the temperatures above 250 °C, even when the catalyst concentration was not so high, for example, in the presence of 1 M KOH[74], or pH 9.5 ~ 9.7[79], or 0.1 to 0.66 M alkali[75], or even in the absence of a mineralizer when the temperature is higher than 300 °C[80], submicrosized or nanosized PZT powders can still be formed. Neither $PbTiO_3$ nor $PbZrO_3$ were detected as a separate phase under such hydrothermal conditions.

Several methods have been developed to synthesize PZT ceramic powders. The comparison of the synthesis routes is listed in Table 1.2

Table 1.2 The comparison of powders synthesis route[81].

Synthesis method	Compositional control	Morphology control	Powder reactivity	Particle size (nm)	Purity (%)	Agglomeration	Calcination step	Milling step	Cost
Solid state reaction	poor	poor	poor	>1000	<99.5	Moderate	yes	Yes	Low moderate
Coprecipitation	good	Moderate	good	>10	<99.5	high	yes	yes	Moderate
Spray / Freeze-drying	Excellent	Moderate	good	>10	<99.9	Low	no	no	Moderate high
Emulsion synthesis	Excellent	Excellent	good	>100	<99.9	low	yes	yes	Moderate
Spray - pyrolysis	Excellent	Excellent	good	>10	<99.9	low	no	no	high
Sol-gel	Excellent	Moderate	good	>10	<99.9	Moderate	yes	yes	Moderate high
Hydrothermal	Excellent	good	good	>10	<99.9	low	no	no	Moderate

1.5 SHAPE FORMING OF PZT AND PLZT CERAMICS

Most ceramics are made by powder processing route and have four steps of powder preparation, shape forming, high temperature sintering and component finishing as shown in Figure 1.19[82].

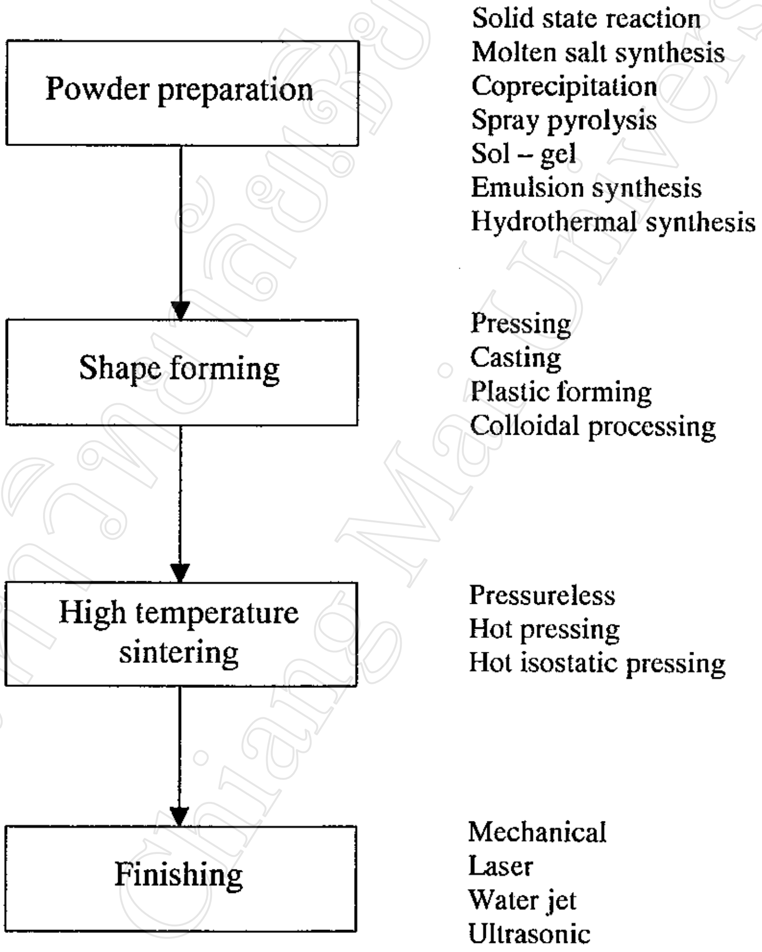


Figure 1.19 Four steps involved in typical powder processing for advanced ceramics[82].

A powder compact is made by dry powder pressing which is accomplished by placing the powder into a die and applying pressure to achieve compaction. The dry powder pressing includes uniaxial pressing, isostatic pressing, and hot pressing. The latter technique combines consolidation and densification in one step.

1.5.1 Uniaxial pressing

This technique is used for parts with length to transverse dimension ratios of less than three. This process allows the fabrication of rather complicated shapes, even with screws or holes perpendicular to the compaction axis, and very high production rates. It involves the compaction of a powder mixture into a rigid die by applying pressure along a single axis through upper and lower pistons[83]. A high pressure, of at least 100 MPa, is necessary to guarantee a high green density. Disadvantage of uniaxial pressing is the non-uniform green density. Fine, dry powder does not flow readily into a mould cavity nor behaves like fluid under compaction because of friction between particles, as well as between the particles and the die walls, prevent easy relative movement of the grains. Consequently, there are density variations throughout the molding, and agglomerates remain as defects in the final product.

1.5.2 Isostatic pressing

Isostatic pressing is one of the shape-forming methods suitable for producing components with complex geometry; it involves the application of pressure equally to the powder from all sides. This essentially gives a more uniform green density. In isostatic compaction, a powder is poured into a rubber bag and stress is applied by means of a liquid that acts as a pressure transmitter. In the wet bag method, the powder is poured into the bag, which is submerged in the liquid (Figure 1.20). After compaction, the bag is withdrawn from the liquid and opened to remove the part. This method is suited to large pieces, but it does not allow high production rates. In the dry bag method, the rubber bag is part of the equipment. The pressure is applied by a liquid on the side of the sample, and by a punch on the top and bottom (Figure 1.20). This method allows for automation in the filling of the mould and the ejection of the sample. Thus, high production rates are possible for small species with relatively simple shapes[84].

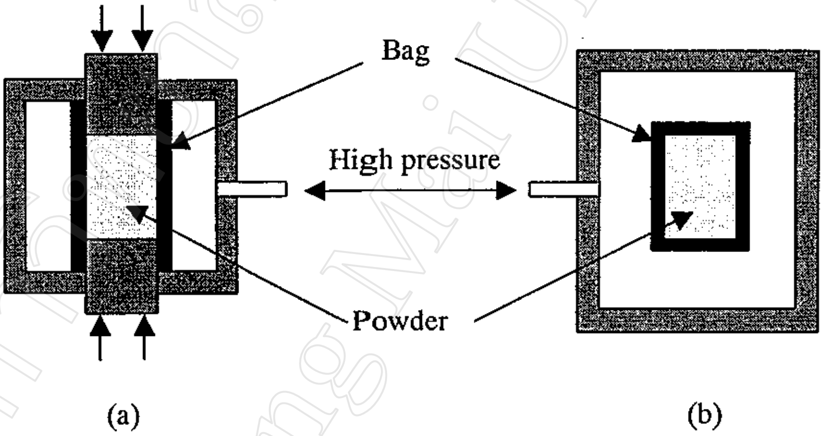


Figure 1.20 Isostatic pressing: (a) dry bag and (b) wet bag method[84].

Dry powder pressing is one of the most popular shape-forming processes, since it involves a relatively simple technology while allowing high production rates. However, the understanding of this process is largely empirical. Most industrial problems in this area are solved by trial and error. Some of the problems encountered include density variations, dimensional control and fracture upon unloading. For example, internal pressure due to the air entrapped within the compact, which causes delamination, may be overcome by de-airing the powder before compaction; optimizing the compaction rate; and in uniaxial compaction, ejecting the sample while keeping a small pressure on it until the air has escaped. Friction stresses on the mould during ejection that may cause defects may be solved by careful control of mould wall smoothness and the use of lubrication[85]. Polymer binders are often used to increase the green strength, and in some cases, to act as a lubricant. Theoretical investigations of these problems has also been described in the literature through both a classic approach by considering the effects of pressure/density relationship, radial pressure coefficient and wall friction coefficient on the compaction behavior and 'mechanical' approach by using continuum mechanics and compute simulation to quantitatively predict the stress and density variations in a shaped mould[84].

1.5.3 Hot pressing process

Pore-free PLZT can be obtained by sintering under atmospheric pressure in air or by applying a vacuum during the early stages of sintering as shown in Figure 1.21. In both the pressureless sintering and hot-pressing routes the sample is surrounded by powders approximating in composition to that of the sample; the correct design of the powder is particularly critical if good quality material is to be made by the pressureless sintering route[19].

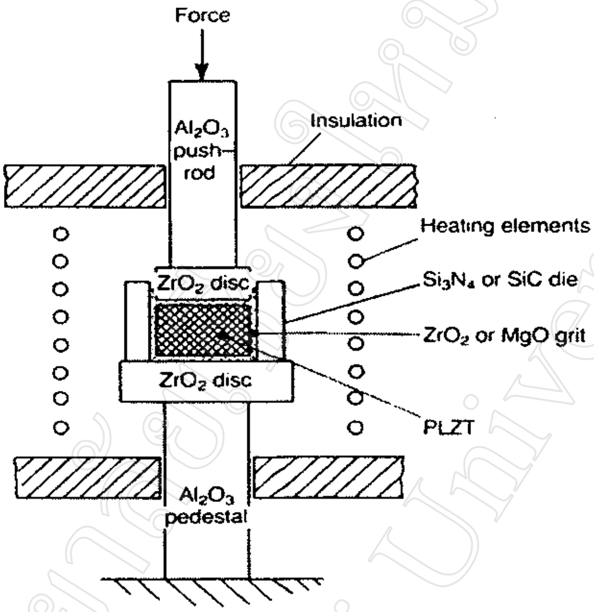


Figure 1.21 Apparatus for hot-pressing PLZT[19].

1.6 OBJECTIVES OF THIS WORK

This thesis concentrates on the synthesis of PZT and PLZT powders and their characterization. The main purposes of this study are ;

1. To study the method of preparing PZT powders by nitrate solutions and hydrothermal process.
2. To characterize the properties of the PZT powders obtained from both processes.
3. To study the effect of calcination temperature of PZT powders synthesized by nitrate solutions.
4. To study the effect of sintering temperature on microstructure of PZT ceramics.
5. To study the effect of La-doped on PZT powders.