CHAPTER 3

SYNTHESIS AND PROCESSING OF FERROELECTRIC PZT POWDERS, CERAMICS AND FILMS

In this chapter, various synthesis routes for PZT powders and fabrication processing techniques for PZT ceramics and films are reviewed. Emphasis is placed on chemical routes, especially the hydrothermal synthesis of PZT powders. The principles of the colloidal chemistry in ceramic suspension and its application to the colloidal processing of ceramics and films, especially when using sub-micron or nano-sized ceramic powders, are given.

3.1. Powder Processing Route for Advanced Ceramics

Although some ceramics may be fabricated by melt processing or by vapour deposition, most ceramics are made by the powder processing route illustrated in Fig. 3.1, which basically involves the four steps of powder preparation, shape forming, high temperature sintering and component finishing [McColm, 1995]. Ceramic powders are therefore crucial to the subsequent processing as well as the properties of final ceramics. The desirable characteristics of ceramic powders include not only a high degree of chemical purity and controlled chemical and phase homogeneity, but also a fine particle size to promote sintering, an equiaxed shape to enhance packing, a narrow particle size distribution to inhibit grain growth, and dispersability to remove defects [Kendall, 1989; Riman, 1995]. In the following section, various synthesis routes for PZT powders will be discussed first.

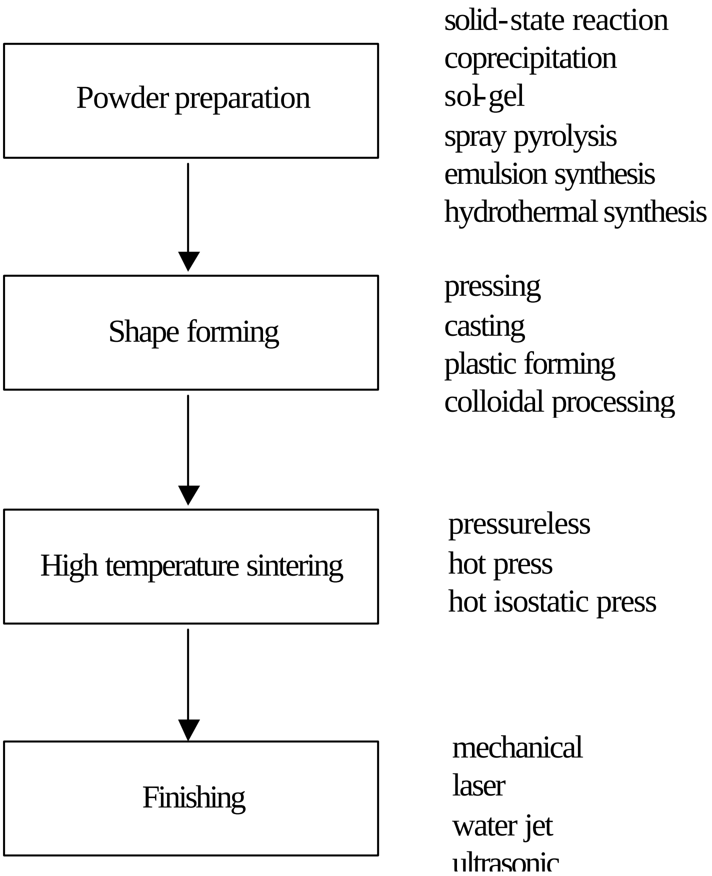


Fig.3.1. Four steps involved in typical powder processing for advanced ceramics.

3.2. Synthesis Routes for PZT Powders

A variety of methods have been developed to synthesise mixed-oxide ceramic powders [Cousin & Ross, 1990]. These methods have become available for both laboratory and industrial production.

Most of them have been used to make PZT powders. A general comparison of the synthesis routes for oxide ceramic powders is listed in Table 3.1.

Table 3.1. Oxide powder synthesis route comparison [Dawson, 1988; Cousin & Ross, 1990]

Synthesis method	**Solid-state Reaction**	**Coprecipita-tion**	**Sol-gel**	**Spray/Freeze Drying**	**Spray Pyrolysis**	**Emulsion Synthesis**	**Hydrothermal Synthesis**
state of development	commercial	commercial	R&D	demonstration	R&D	demonstration	demonstration
compositional control	poor	good	excellent	excellent	excellent	excellent	excellent
morphology control	poor	moderate	moderate	moderate	excellent	excellent	good
powder reactivity	poor	good	good	good	good	good	good
particle size (nm)	>1000	>10	>10	>10	>10	>100	>100
purity (%)	<99.5	>99.5	>99.9	>99.9	>99.9	>99.9	>99.5
agglomeration	moderate	high	moderate	low	low	low	low
calcination step	yes	yes	yes	yes	no	yes	no
milling step	yes	yes	yes	yes	no	yes	no
costs	low-moderate	moderate	moderate-high	moderate-high	high	moderate	moderate

3.2.1. Solid-State Reaction

The most direct method of making mixed-oxides 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 consecutive steps of mixing, solid-state reaction and milling. Particles can be formed either in a structured fashion or randomly. Then 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 comminution process to reduce the particle size to the micrometre level. But, milling to particle size below 1 μm is technically difficult for some hard materials, contaminates the product and is energy intensive [Greskovich, 1976]. The homogeneity and purity of the powder thus 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 [Cramer, 1995].

3.2.1.1. Conventional 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 [1965], there are four regions corresponding to four chemical processes during calcination (see Fig. 3.2), i.e.

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 [Xu, 1991].

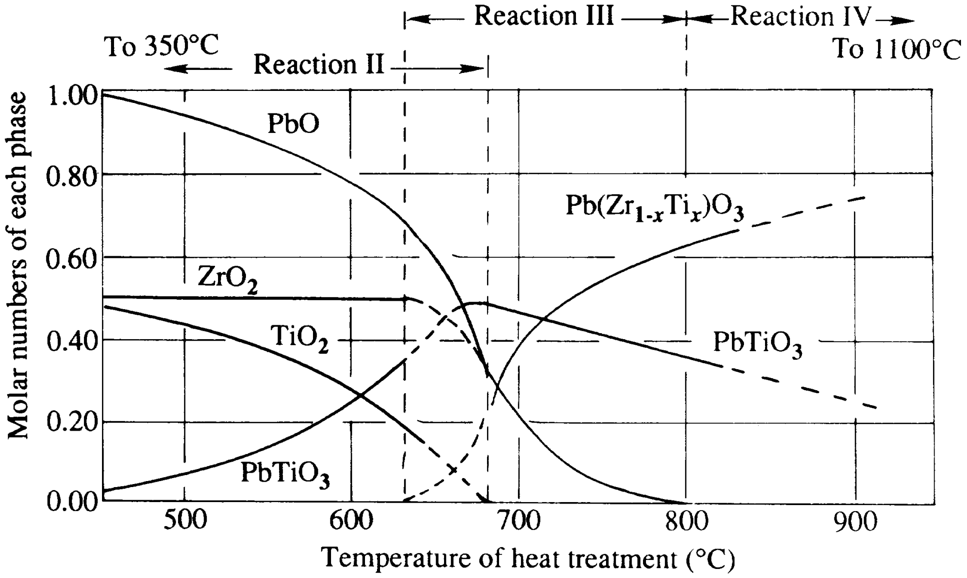


Fig. 3.2. Four regions of solid-state reaction appear as the calcination temperature increases [After Matsuo & Sasakki, 1965].

As shown in Fig. 3.2, the reaction mechanism of the conventional one-stage solid-state reaction leading to PZT solid-solution formation actually involves in several steps, with $PbTiO_3$ (denoted as PT) formation at an early stage of the reaction followed by some intermediate phases formation [Chandratreya *et al.*, 1981; Hiremath *et al.*, 1983]. The conversion of the intermediate phases into

PZT involves long-range diffusion resulting in compositional fluctuation [Kakegawa *et al.*, 1977]. 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 volatilisation temperature of PbO. However, Kakegawa *et al.* [1988] 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 [Shirasaki *et al.*, 1973]. Therefore, an improved two-stage solid-state reaction process has been proposed.

3.2.1.2. Improved two-stage solid-state reaction process

In this process, $(Zr_{1-x}Ti_x)O_3$ powder (denoted as ZTO) is synthesised as the first step, followed by solid-state reaction between ZTO and PbO powder, which eliminates (or suppresses) 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: $(1-x)\ ZrO_2 + x\ TiO_2 \rightarrow Zr_{1-x}Ti_x\ O_4$ (ZTO);

stage II: $ZTO + PbO \rightarrow PZT$.

The ZTO powder can be prepared either by conventional solid-state reaction route [Shrout *et al.*, 1990; Yamamoto, 1992] or by chemical synthesis routes, such as coprecipitation [Singh *et al.*, 1993], spray pyrolysis [Kakegawa *et al.*, 1988], melt salt synthesis [Kimura *et al.*, 1992], and hydrothermal process [Yamamoto *et al.*, 1989; Kulig *et al.*, 1995]. By using this two-stage process, compositionally homogeneous PZT powders can be synthesised at lower calcination temperatures (e.g. 600°C) and in shorter calcination duration. The resulting PZT powders are more sinterable due to the “reactive *et al.*, 1991] 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 Fig. 3.3) [Shrout *et al.*, 1990]. The highly reactive powders allow densification at temperatures 100 to 200°C lower than that reported for conventionally one-stage process [Fukai *et al.*, 1990; Shrout *et al.*, 1990].

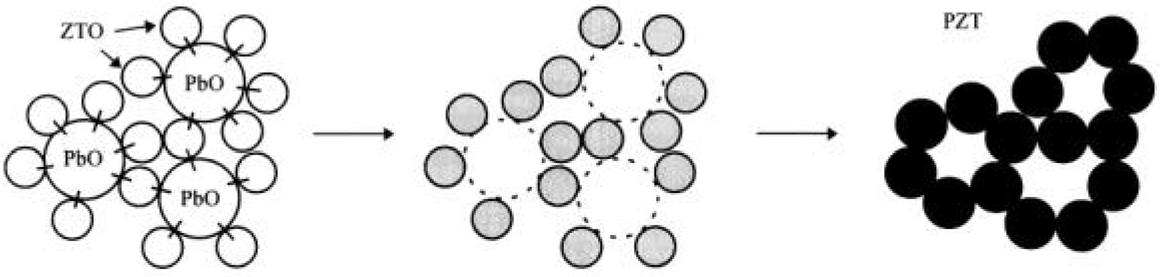


Fig. 3.3. Schematic representation of the perovskite PZT powder formation process via two-stage solid-state reaction and associated morphological change [After Shrout *et al.*, 1990].

3.2.2. 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 [Segal, 1989]. A number of chemical synthesis methods have been used to make PZT powders, such as coprecipitation, sol-gel, melt salt, spray pyrolysis and hydrothermal synthesis, which will be discussed in the following sections.

3.2.2.1. Coprecipitation from solution

Coprecipitation from solution is one of the oldest 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 good. 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 [Geiger, 1995]. It has been reported for making PZT powders in combination with spray and freeze drying techniques since 1960’s [McNamara, 1965; Thomson, 1974; Murata *et al.*, 1976; Biggers & Venkataramani, 1978; Duran & Moure, 1985]. Spray drying is a technique which consists of a rapid vaporisation of the solvent contained in small droplets of the required solutions of cations, whereas freeze drying utilises slow sublimation of the solvent. These techniques afford excellent control over impurity levels and compositions, and generate homogeneous fine particles. Utilising rapid vaporisation or slow sublimation of the solvent, they reduce the agglomeration problem associated with the large surface tension of vapour-liquid interface. PZT powders of adequate purity, homogeneity and stoichiometry have been made [Lal & Krishnan, 1987]. 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 [Schwartz *et al.*, 1988]. Wang *et al.* [1992] 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.* [1993], 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, viz., 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 optimise the pH for the coprecipitation of the ternary Pb-Zr-Ti system [Choy *et al.*, 1995].

3.2.2.2. 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. The solubilities of oxides in molten salt vary greatly, from less than 1×10^{-10} mole fraction to more than 0.5 mole fraction, typically 1×10^{-3} to 1×10^{-7} mole fraction. However, because of the small diffusion distances in an intimate mix of the constituent oxides in the molten salt, and the relatively high mobility of species in the molten salt (1×10^{-5} to 1×10^{-8} cm^2/sec compared with as little as 1×10^{-18} cm^2/sec in the solid state), 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 hour, but a small amount of ZrO_2 residue was found due to the incomplete reaction [Arendt *et al.*, 1979]. However, since morphology control of electroceramic powders is possible by this process [Kimura & Yamaguchi, 1987], it has been used to prepare needle-like PZT powders [Kimura *et al.*, 1992].

3.2.2.3. 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 (e.g.>300°C) to form the desired inorganic phase by pyrolysis [Messing *et al.*, 1993]. During spray pyrolysis, the solution is atomised 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, thermolysis (i.e. 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 compartmentalising 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 [Kim et al, 1995; Faber *et al.*, 1995]. 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.

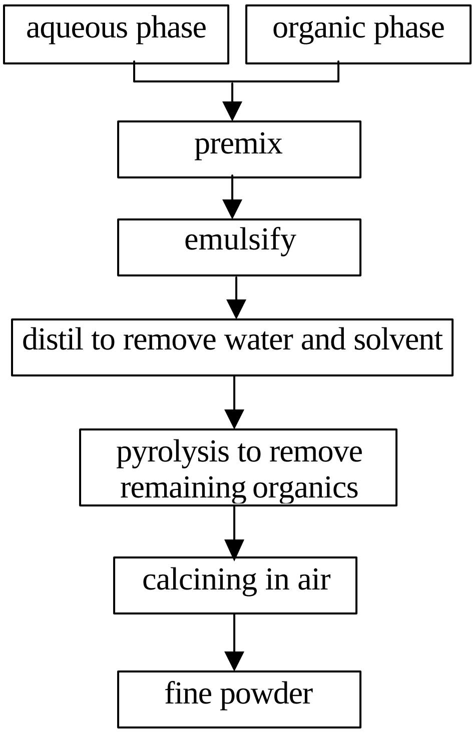
3.2.2.4. Sol-gel

The sol-gel processing consists of the formation of an amorphous gel from solutions followed by dehydration at relatively low temperatures. 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 hydrolysed which leads to branching and crosslinking. This polymerisation reaction forms three-dimensional structures and avoids any segregation phenomena. Then the rigid coherent gel is dried and heated at temperatures dramatically lower than with other techniques. The sol-gel method can produce high quality fine electroceramic powders with excellent homogeneity but the process is tedious and expensive because of the scarce 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 [Ogihara *et al.*, 1988; Hirashima *et al.*, 1990] or by non-alkoxide sol-gel methods [Zhuang *et al.*, 1988; Ostertag *et al.*, 1989], this method is, so far, not as successful in making PZT powders as in making PZT thin films. This is due to many R & D activities directed at the development of ferroelectric PZT thin films for use as high capacity non-volatile memories (NVMs) and high capacity dynamic random-access memories (DRAMs) in recent years [Swartz *et al.*, 1997].

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 [Wilkinson *et al.*, 1994]. 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 [Polli & Lange, 1995]. This effect is certainly easier to control in relatively small-dimensional thin films than that in relatively large-dimensional powders.

3.2.2.5. Emulsion synthesis

The flow chart of emulsion process is shown in Fig. 3.4. The process is generally applicable for many ceramic powders or combinations of ceramic powders for which water-soluble precursors are available [Mahr *et al.*, 1993]. 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 minimised agglomeration at a relatively moderate cost. However, few studies have been reported for making PZT powders by this process [Cipollins, 1987], probably because it encounters similar problems to those in sol-gel processing.



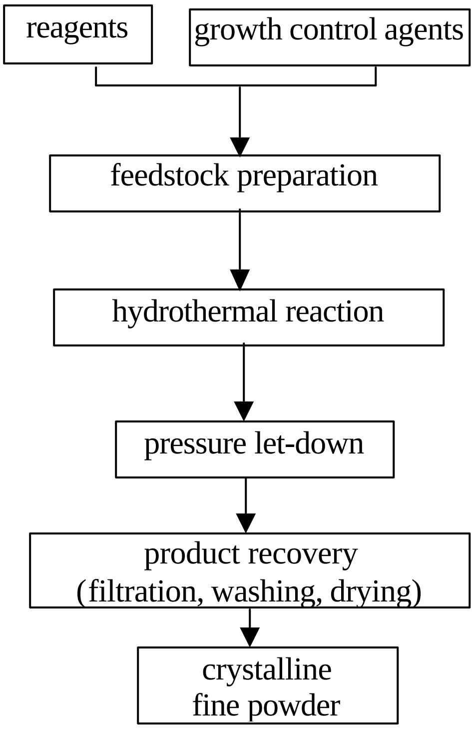


Fig. 3.4. Flow chart of emulsion process [After Mahr *et al.*, 1993].

Fig. 3.5. Flow chart of hydrothermal synthesis [After Dawson, 1988].

3.2.2.6. Hydrothermal synthesis

Hydrothermal synthesis can be defined as the treatment of aqueous solutions or suspension of precursors at elevated temperature in pressurised vessels [Laudise, 1987]. 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. 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-stabilising phases that might not be stable at atmospheric conditions [Riman, 1995]. A generalised flow chart of this process is shown in Fig. 3.5.

The basic mechanism for the hydrothermal formation of ceramic oxide particles is described as a dissolution/precipitation and/or *in-situ* transformation process (Fig. 3.6). 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. In many cases, however, the suspended solids are not soluble enough in aqueous solution, and hence, either mineralisers 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 [Nishizawa *et al*., 1982]. In some cases, both mechanisms might be in operation depending on the synthesis conditions [Watson *et al.*, 1987; Eckert *et al.*, 1996]. The hydrothermal synthesis of ceramic powders possesses two major advantages: the elimination or minimisation 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 and is explained in more detail in Section 3.2.3. Thus, it is particularly suitable for preparing electroceramic powders such as PZT.

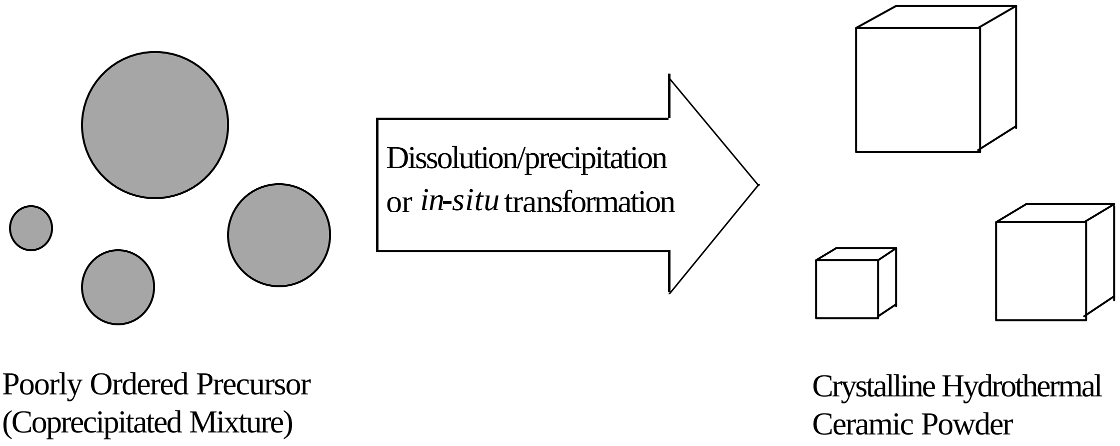


Fig. 3.6. Hydrothermal dissolution/precipitation and/or *in-situ* transformation process [After Dawson, 1988].

3.2.3. Hydrothermal Processing

3.2.3.1. Features of hydrothermal processing

The features of hydrothermal processing as applied to ferroelectric ceramic powders are summarised as follows [Ponton, 1993]:

(1) 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.

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

(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, for example, can be grown to submicron- or even nano-metre size by control of the nucleation and growth processes.

(5) The powders synthesised by the hydrothermal process are more reactive toward sintering and often no presintering or calcination stages are needed. 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 process utilises comparatively inexpensive precursor chemicals such as oxides, hydroxides, chlorides, acetates and nitrates rather than alkoxides.

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

(8) The disadvantages of the process involve the moderately high initial cost of the apparatus, safety issues related to high pressure processing, and potential high temperature corrosion problems arising from the presence of basic or acidic mineralisers.

In spite of that, the worldwide interest in hydrothermal synthesis for the production of PZT powders has grown since the late 1980's. Table 3.2 lists some of the examples of recent research and development in this field.

Table 3.2 . Recent R&D on the hydrothermal processing of PZT powders.

Time	**Researcher(s)**	**Affiliation**	**Materials**
1988	W.J.Dawson	Battelle Columbus Division/USA	PZT
1990	T.Ichihara *et al.*	Tokyo Institute of Technology/Japan	PZT
1990	T.Yamamoto *et al.*	National Defense Academy/Japan	Nb_2O_5 modified PZT
1992	C.E.Millar *et al.*	Ferroperm AS/Denmark	modified PT
1993	S.Komarneni & R.Roy	Penn State University/USA	PZT, PLZT
1994	K.Lubitz *et al.*	Siemens AG/Germany	PZT
1994	B.Thierry *et al.*	University de Valenciennes/France	PZT
1994	J.P.Witham *et al.*	Penn State University/USA	PZT
1994	C.H.Lin *et al.*	National Tsing Hua University/Taiwan	PZT, PLZT
1994	H.Cheng *et al.*	Perking University/China	PZT
1995	M.M.Lencka *et al.*	Rutgers University/USA	PZT
1996	Ohba *et al.*	Tokyo Institute of Technology/Japan	PZT

3.2.3.2. Hydrothermal synthesis of PZT powders

The most commonly used precursors for the hydrothermal synthesis of PZT powders are nitrates, chlorides, oxychlorides, acetates, hydroxides, and in some cases, Zr or Ti alkoxides. Table 3.3 summarises the hydrothermal synthesis conditions and characteristics of the resulting PZT powders as reported in the literature. 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.* [1990] 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 electric properties [Lin *et al.*, 1993] and to produce a lower agglomeration state [Lemoine *et al.*, 1995].

The use of a catalyst or mineraliser for PZT powder synthesis is necessary as 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 [Beal, 1987], 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 [Beal, 1987]. 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 (e.g. < 2 M), and PZT was produced at higher KOH concentrations (e.g. > 4 M) and formed very quickly in 10 M KOH solution [Lee *et al.*, 1987]. Since the individual Pb, Ti, and Zr ion species have different solubility behaviours 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 [Lemoine *et al.*, 1995].

Another important factor which influences the hydrothermal formation of PZT powder is temperature. Temperature and mineraliser 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 [Shimomura *et al.*, 1991]. 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 [Cheng *et al.*, 1993]. PZT can be detected by X-ray diffraction when hydrothermally synthesised 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 [Lee *et al.*, 1987]. At the temperatures above 250°C, even when the catalyst concentration was not so high, for example, in the presence of 1 M KOH [Lemoine *et al.*, 1995], or pH9.5 ~ 9.7 [Witham *et al.*, 1994], or 0.1 to 0.66 M alkali [Beal, 1987], or even in the absence of a mineraliser when the temperature is higher than

300°C [Kutty *et al.*, 1984], submicron or nanosized PZT powders can still be formed. Neither $PbTiO_3$ nor $PbZrO_3$ were detected as a separate phase under such hydrothermal conditions.

Table 3.3. Synthesis conditions and characteristics of hydrothermally processed PZT powders.

Precursor Chemicals	**Concentration**	**Catalyst/ Mineraliser**	**Temperature(°C)**	**Time (hour)**	**Powder Characteristics**	**Reference**
$TiOCl_2$ $ZrOCl_2$ PbO	Ti/Zr=0 to 1		150~400	6~8	well defined aciculate crystals of PZT are formed above 300°C	Kutty, et al, 1984
$TiCl_4$ $ZrOCl_2$ PbO	Ti/Zr=1 10% Pb excess	0.56 N halide 0.1~0.66N alkali	300	0.5	low mineraliser concentration yield either submicrometer rounded or cubic particles up to several micrometers. While high concentration led to the product with random morphology	Beal, 1987
$Pb(NO_3)_2$ $ZrOCl_2.8H_2O$ $TiCl_4$	22% excess Pb	4~10 M KOH	70~200	0.5~48	particle size 1-3 μm, cubic, grain size decreases with the increase of temperature	Ichihara, *et al.*, 1990
$Pb(NO_3)_2$ $ZrOCl_2.6H_2O$ $TiCl_4$ $NbCl_5$	$Pb(Zr_{0.53}Ti_{0.47})O_3$ +x Nb_2O_5 (x=0.0025, 0.005, 0.01, 0.015)	KOH	180	5	particle size 0.75~0.79 μm, specific surface area 6.4~6.7 g/m^2, improved electric properties with Nb_2O_5 addition	Yama-moto, *et al.*, 1990
$Pb(CH_3COO)_2$ $ZrOCl_2$ $Ti(OC_4H_9)_4$	Pb/(Zr+Ti)=1~1.9, Zr/Ti=0/10~10/0	1~5 M KOH	100~200	2	PZT in MPB zone was found at Zr/Ti=5/5, 5M KOH, 200°C/2h	Cheng, *et al.*, 1993
$Pb(CH_3COO)_2$ $ZrOCl_2$ $Ti(OH)_4.xH_2O$	$Pb(Ti_{1-x}Zr_x)O_3$, x=0.52~0.64	NaOH	200	24	particle size 0.2 μm, decreases with x, cubic, more sinterable (1100°C)	Lin, *et al.*, 1994
$Pb(CH_3COO)_2$ $ZrOCl_2.8H_2O$ $Ti(OH)_4.xH_2O$	$Pb(Ti_{0.48}Zr_{0.52})O_3$, 5, 10, 20 mole% excess Pb	NaOH	200		particle size 40 nm, spherical or elliptical shape, lowest resistivity and highest dielectric constant with 20% of excess Pb	Lin, *et al.*, 1993
$Pb(CH_3COO)_2.3H_2O$ $ZrOCl_2.8H_2O$ $Ti(OH)_4$ $La(CH_3COO)_3.3/2H_2O$	$Pb(Ti_{0.48}Zr_{0.52})O_3$ 0~5 mole% La substitution for Pb	3 M NaOH	200	24	single tetragonal PLZT phase, addition of La ions reduces the particle size from 0.5 to 0.3 μm (La from 0~5 mole%)	Lin and Pei, 1993
$Pb(NO_3)_2$ $ZrOCl_2.8H_2O$ $TiCl_4$	$Pb(Ti_{0.48}Zr_{0.52})O_3$	KOH	200	0.5~1	PZT formed in two KOH concentration range: 0.18±0.08 mol/L and >2 mol/L, cubic, 0.3~0.5 μm	Hu, *et al.*, 1994
$Pb(NO_3)_2$ $ZrOCl_2$ $TiCl_4$	Pb/Zr=1.5/0.52	10 M KOH with microwave (2.45 GHz, 630±50 w)	115~164	0.5~1	particle size 3~5 μm, faster but with larger size	Komarnni *et al.*, 1993
Pb nitrate Zr nitrate Ti alkoxide	$Pb(Ti_{0.46}Zr_{0.54})O_3$, Pb/(Zr+Ti)=1~1.5	PH=13 1 N KOH 1 N NaOH	180~300	1	PZT powder formed when temperature above 250°C, cubic shape when KOH used and tabular when NaOH used	Lemoine, *et al.*, 1995

Precursor Chemicals	**Concentration**	**Catalyst/ Mineraliser**	**Temperature(°C)**	**Time (hour)**	**Powder Characteristics**	**Reference**
$Pb(CH_3COO)_2.3H_2O$ Zr or Ti propoxides or isopropoxides		PH=9.5~9.7	250~300	4~6	nanosized powder, sintering at 1200°C, 95% theoretical density	Witham, *et al.*, 1994
Titania gel Zirconia gel $Pb(NO_3)_2$	Zr/Ti=1.08	KOH	150~180	4	PZT powders with size from 0.8 to 10 μm, morphology from cubic to round shape depending on the Pb and KOH concentrations	Ohba, *et al.*, 1996

3.3. Shape Forming of PZT Ceramics

3.3.1. Conventional Shape Forming Methods

3.3.1.1. Dry powder pressing

Traditionally, 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. This technique includes uniaxial pressing, isostatic pressing, hot pressing and hot isostatic pressing. The latter two techniques combine consolidation and densification in one step.

Uniaxial pressing 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 punches (or pistons) [Richardson, 1992]. A high pressure, of at least 100 MPa, is necessary to guarantee a high green density. A 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 moulding, and agglomerates remain as defects in the final product.

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 (Fig.3.7). 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 (Fig. 3.7). 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 [Bortzmeyer, 1995].

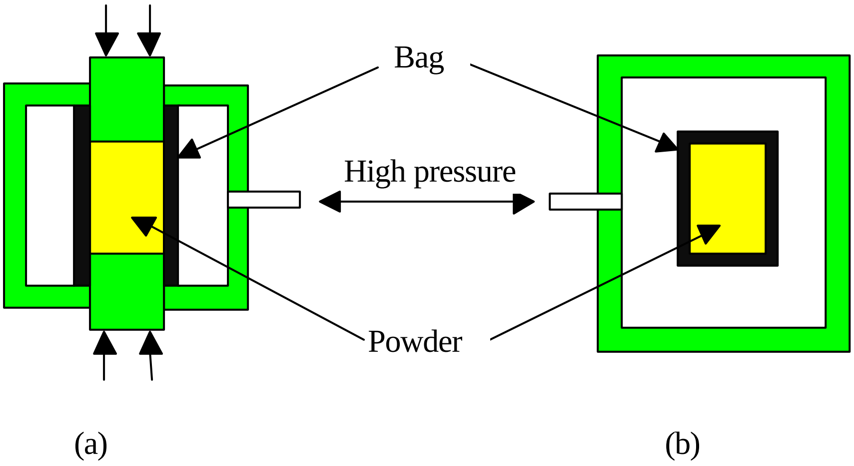


Fig. 3.7. Isostatic pressing: (a) 'dry bag' and (b) 'wet bag' method [After Bortzmeyer, 1995]

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; optimising 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 which may cause defects may be solved by careful control of mould wall smoothness and the use of lubrication [Lewis, 1996]. 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 behaviour and 'mechanical' approach by using continuum mechanics and compute simulation to quantitatively predict the stress and density variations in a shaped mould. A good review of such theories has been given by Bortzmeyer [1995].

3.3.1.2. Slip casting and tape casting

Slip casting is one of the shape-forming techniques used for traditional ceramics. It has been applied to advanced ceramics as well because it permits the formation of complex geometry components. The basic slip casting process employs ceramic particles suspended in fluids containing polar molecules to form what is called a slip, which is cast into a porous mould so that the liquid is drawn out by capillary action to leave a solid deposit of ceramic particles on the mould surface [Richardson, 1992]. Generally, the fluid is water and the mould is plaster of Paris. This is a cheap process and is suitable for making large and complex thin-walled items with uniform wall thickness. However, the primary disadvantage of the process is its lack of precise dimensional control. Furthermore, the properties of the final product are rarely better than those of pressed materials because flocculation occurs as a result of the van der Waals attractive force between the particles, causing aggregation, shrinkage and cracking.

Investigations of the mechanism of formation of solid casts from slips have shown that it is a diffusion-controlled process and amounts to a simple dewatering of the slip [Cowan, 1976]. The driving force for this process is the suction pressure created by the porous plaster mould. When a slip is first poured into a mould, a high rate of casting is observed for a few seconds. This is due to the high rate of water diffusion through the plaster. Following the initial stage, the rate of cast formation is determined by the permeability of the solid cast. It has been shown [Adcock & McDowall, 1957] that the rate of cast formation can be quantitatively determined by

$$\frac{L^2}{t} = \frac{2PgE^3}{5S_p^2\eta(y-1)(1-E)^2} \tag{3.1}$$

where L is the thickness of the cast layer, t is time, P is the suction pressure, E is the void fraction, S_p is the surface area of solid particles, η is the viscosity of fluid, y is the volume of slip containing 1-E volume fraction of solids, and g is acceleration due to gravity.

From the above equation it is apparent that the rate of casting can be increased if the pressure on the slip is increased. This has led to the development of other two novel casting processes: pressure slip casting (or pressure filtration) and centrifugal casting. Both processes give increased casting rates and green compacts possessing low porosity, a narrow pore size distribution and essentially zero shrinkage on drying compared to conventional slip casting [Fennelly & Reed, 1972; Lange & Miller, 1987; Huisman *et al.*, 1995].

Tape casting is another shape-forming technique, mainly used for thick film and tape preparation [Mistler, 1990]. The process involves suspending finely divided ceramic powders in aqueous or non-aqueous liquid systems comprised of solvents, plasticizers and binders to form a slurry. A green sheet is formed by passing the slurry under a doctor blade on to a carrier (Fig. 3.8). The most simple form of type casting system consists of an open-based reservoir which sits upon the carrier. One side of the reservoir is recessed with a tapered edge to form a blade. Often, a two-blade device is used in which both blades are adjustable for height. This attempts to give better control over the flow under the casting blade. In most continuous casting processes, slip is pumped to the casting head thereby keeping a constant pressure at the blade. When the solvents evaporate, the fine, solid particles coalesce into a relatively dense, flexible sheet that may be stored on take-up reels or stripped from the carrier in a continuous sequence. This process has become established for manufacturing a variety of electroceramics [Hyatt, 1995]. Typical applications include the preparation of capacitors, piezoelectric devices, ferrite memories, electrically insulating substrates for thick and thin film circuitry. As a basic ceramic forming method it is generally advantageous for preparing large area, thick films of uniform and high green densities. Complex shapes with intricate hole patterns can be formed directly by punching or stamping the parts from the as-cast sheet.

3.3.1.3 Extrusion and injection moulding

There are two main plastic forming or shaping methods: Extrusion and injection moulding. They involve producing a shape from a mixture of powder and additives that is deformable under pressure.

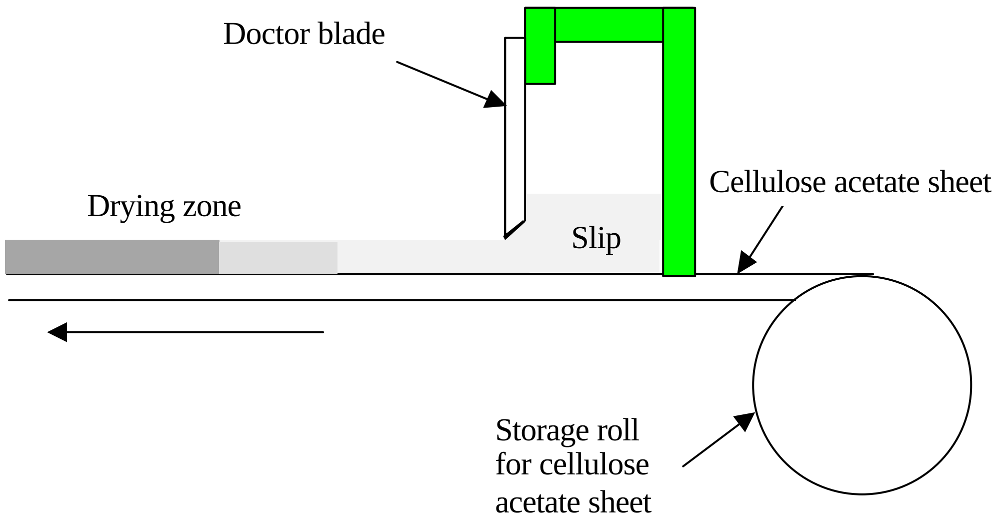


Fig. 3.8. A typical doctor blade arrangement [After Mistler, 1995].

Extrusion is a plastic forming technique which is used extensively for the fabrication of tubes, rods and other elongated shapes that have a constant cross-section. The body is plasticized with an organic binder, which is partially hardened by drying at low temperatures, so that it can be squeezed through a nozzle in an extruder. This requires a relatively high organic content. As a consequence, the green part has a low ceramic content and the resulting product has a relatively low strength. Dimensional changes are due to the shrinkage, which occurs due to softening and flow which occurs in the green part under its own mass during drying and removal of the organic binder system [Benbow & Bridgwater, 1993].

Injection moulding is another high-volume production technique for making net-shape or near-net-shape parts. It involves forcing a deformable mixture of powders, additives and binders through an orifice via a narrow passageway into a tool cavity where it hardens; the resultant green part can then be removed. The parts are heated to drive off the organic binder, and subsequently sintered [Mutsuddy & Ford, 1995]. This method, which is well known for producing plastic parts, is probably the most interesting method for mass producing small and medium sized parts having a complex geometry, but it has been proven difficult to achieve in ceramics. The main problem is the large polymer content (typically 35 ~ 40 vol.%) that must be slowly removed prior to high temperature sintering in order to prevent cracking. In addition to the restrictions and economic concerns relating to their potential or actual toxicity, the polymer binders and plasticizers used in injection moulding possess several processing problems with respect to incomplete burn-out, resulting in residual impurities and defects, and the need for long burn-out times, especially for large cross-section products. During the removal of additives, the ceramics may undergo substantial shrinkage and distortion from the desired shape. Another problem is that of moulding defects associated with the mould-filling step of injection moulding. The competitive processes of heat transfer and fluid flow work against one another [White & Dee, 1974]. The injection moulding mix should be as fluid as possible to make filling of the mould easy; this implies that the mix should be significantly overheated, and yet must cool relatively quickly to become more viscous and hence harden to a solid, setting the part in the mould. The result of this competition between the two processes is often the creation of defects in the as-moulded part [Janney, 1995]. Therefore, novel processing approaches, such as gel casting [Omatete *et al.*, 1991] and direct coagulation casting [Graule *et al.*, 1995a], are needed to overcome these problems by separating the mould-filling operation from the setting operation.

3.3.2. Colloidal Processing

3.3.2.1. Advantages of colloidal processing

Agglomeration is a natural process for all ceramic powders because the van der Waals forces acting between the solid particles are always attractive, and become particularly significant for nano- or submicron-sized powders due to their extremely high surface area. This is the major factor responsible for the inhomogeneities in ceramic microstructures, which results in reduced reliability as well as poorer mechanical and electrical properties for structural and functional ceramics, respectively. It has been shown that agglomerates can form by various means, e.g. by drying a suspension, by colloidal destabilisation of a suspension, or by dry-pressing a powder [Kendall *et al.*, 1990]. Such agglomerates are generally too strong to be broken down through subsequent shearing or by ultrasonic agitation in conventional shape forming techniques. One effective method of minimising the number and size of agglomerates, and also of mixing powders homogeneously, is to disperse particles by suspending them in a liquid. This is so-called colloidal processing.

It has been well demonstrated that colloidal processing methods offer potential advantages over conventional powder processing routes as regards increasing the reliability of advanced ceramics. This is achieved by minimising the number and size of the undesired heterogeneities and improving the chemical homogeneity at the submicometre scale during fabrication [Lange, 1989]. The colloidal processing approach for fabricating ceramics involves: (1) the formulation, de-agglomeration and stabilisation of the colloidal ceramic powder (10 nm to 10 μm) slurry, (2) consolidation of the slurry to pack the particles to a high density, and (3) densification, after drying, by heat treatment. By controlling the particle interactions through colloidal chemistry, the agglomeration process can be prevented by stabilising the ceramic suspension against flocculation. Thus, the resulting ceramic products are much improved.

Alford *et al.* [1987, 1988] reported a viscous polymer processing (VPP) route which involves the use of special polymers to aid disaggregation of powder agglomerates. The viscous polymer solution acts not only as a role to transfer significant stress to the powder agglomerates but also as a lubricant between the particles. This enables the agglomerates to be broken down more easily and thus to give more homogeneous microstructure of ceramics. Improved results with reduced sintering temperature and high strengths have been reported for both structural and functional ceramics. For example, viscous processed alumina could be sintered at a temperature of 1200°C and strength above 1 GPa obtained [Alford *et al.*, 1987, 1988]. Similar results have been shown for PZT ceramics [Pearce *et al.*, 1996]. This processing, however, mainly relies on viscous polymer solutions and strong mechanical shear force to break down the agglomerates. When the particle size is decreased to submicron or even nonometre range, large amount of polymers will be needed to cover the large surface area. Consequently, problems associated with low compaction density and long debinding time will arise. If, however, the particle surface could be modified chemically rather than merely physically, the compaction of the particles will become more efficient.

3.3.2.2. Interactions of colloidal particles in aqueous solution

When a particle is immersed in an aqueous solution, it usually acquires a surface charge, either by adsorbing or desorbing ions according to some chemical equilibrium with the surrounding solution. For example, the surface of an oxide particle is hydroxylated when coming into contact with water, and undergoes proton association-dissociation reactions of the form:

$$\text{(low pH)}\ -M^{+}-OH_2 \xleftarrow{H^{+}} -M-OH \xrightarrow{OH^{-}} -M-O^{-} + H_2O\ \text{(high pH)}$$

where -M represents the metal atom. Thus the surface is positively charged at low pH and becomes negative at high pH. At a certain pH which is called the point of zero charge (PZC) (or the isoelectric point (IEP) if determined from electrokinetic measurement), the total charge on the surface is zero and the electric repulsion between two such surfaces is eliminated.

The ions of opposite charge which are dissolved in water, known as counterions, are attracted towards the surface. However, they do not simply stick to the surface, but form a diffuse layer of charge adjacent to the surface due to the balance between their electrostatic and entropic energy. The surface charge plus the diffuse layer of opposite charge constitute an electric double layer (Fig. 3.9).

When two particles approach each other, the two double layers interpenetrate, causing a repulsive force between them. Meanwhile, van der Waals attractive potentials also act on the particles but on a much short range. The interaction of these long- and short-range potential can be described approximately by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [Hiemenz, 1977; Hunter, 1989]. The heory

[After Shaw, 1971].

Depending on the electrolyte concentration and surface charge density or potential, the particles can either be stable or coagulate in a suspension. The main factor inducing two surfaces to come into adhesive contact in a primary minimum is the lowering of their surface potential or charge, brought about by increased ion binding and/or increased screening of the double-layer repulsion by increasing the salt concentration. However, if the surface charge remains high on raising the salt concentration, two surfaces can still adhere to each other, but in a secondary minimum, where the adhesion is much weaker and easily reversible.

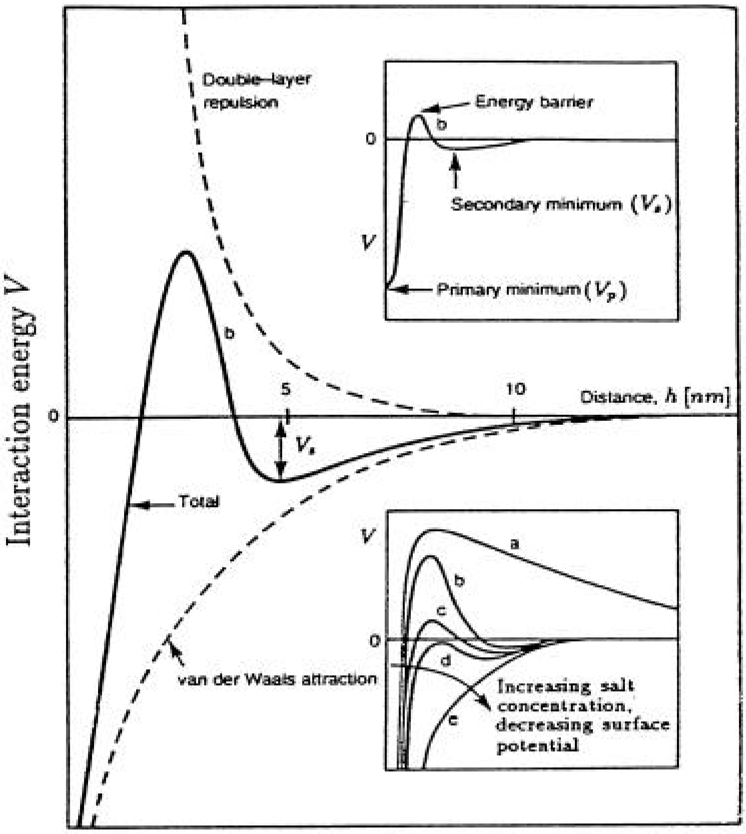


Fig. 3.10. Schematic particle interaction energy versus particle surface separation distance curve according to DLVO theory [After Israelachvili, 1991]. (a) Surfaces repel strongly; small colloidal particles remain 'stable'. (b) Surfaces come into stable equilibrium at the secondary minimum if it is etically stable'. (c) Surfaces come into the secondary minimum region; colloids coagulate slowly. (d) At the 'critical coagulation concentration', surfaces may remain in the

secondary minimum region or move closer together and adhere; colloids coagulate rapidly. (e) Secondary minimum region absent; colloids coalesce immediately.

3.3.2.3. Controlling interparticle forces

It has been shown that well dispersed state of colloidal particles will give a low viscosity suspension and high packing density after consolidation [Aksay & Kikuchi, 1986; Lange & Miller, 1987]. But the behaviour of suspensions during handling is strongly affected by the interaction between the particles. If the interactions are mainly repulsive, and if the suspended particles are small, the system does not change with time and is called colloidally stable. If, however, attraction between the particles prevails, the particles agglomerate, the suspension flocculates (or coagulates) and macroscopic phase separation results rapidly. Stable dispersions can be created by manipulation of interparticle forces via either the electrical double layer or by using large molecules.

Particles suspended in an aqueous solution generally experience a double-layer repulsion, and this repulsion can be controlled by changing the solution condition. For most ceramic materials the surface charge will depend on pH, typically being positive in acidic conditions and negative when the solution is alkaline. At the IEP, the double-layer repulsion will vanish, which provides a common method for coagulating suspensions. Stability is maximised by operating at a pH far from the IEP. The range of the double-layer repulsion is also reduced by increasing salt concentration as shown in Fig. 3.10. In a concentrated salt solution the range can be short enough to allow a secondary minimum in the force at a finite separation. This can be very convenient because it allows reversible coagulation, and it allows compaction to a high volume fraction by avoiding the open floc structures associated with strong attraction into a primary minimum [Horn, 1995]. However, while the double-layer repulsion is very flexible and easy to modify, there are situations where particle size is either too large or the particles too heavy, or the particle surface charge is too low or unstable, in which the double-layer repulsion is not strong enough to stabilise a suspension.

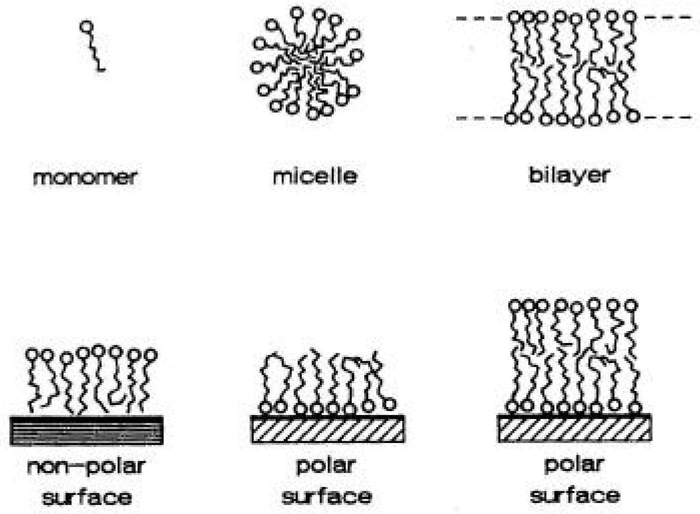


Fig. 3.11. Representation of the behaviour of amphiphilic molecules known as surfactants. One end of the molecule (shown as a small circle) is a polar ‘head’, and likes to be in or adjacent to polar media such as water. The other end (shown as a zigzag line) is a non-polar ‘tail’, typically a hydrocarbon chain, which prefers to be in a non-polar environment. These requirements can be met by surfactant molecules associating in solution, or by adsorbing with appropriate orientation to surfaces [After Horn, 1995].

An alternative way to modify the particle surface is using surfactants. Surfactants are classified as macromolecule dispersants with molecular weight usually less than 1000, and with a polar functional group or groups. Because they are amphiphilic, having a polar or hydrophilic ‘head’ which is soluble in water but not in oil, and a non-polar ‘tail’ which is hydrophobic, preferring a non-polar environment to water, when present in solution, surfactants readily adsorb to surfaces, generally with the hydrophilic end down if it is polar and the hydrophobic end down if it is non-polar (Fig. 3.11), thereby changing the surface state. For example, hydrophobic particles in water might have a low surface charge and be pulled together by the hydrophobic attraction so that they aggregate, making it difficult to form a stable suspension. However, an appropriate amount of ionic surfactant dissolved in the water would adsorb to the particles with its hydrophobic ‘tails’ down, forming a monolayer and exposing charged head-groups to the aqueous phase. This would remove the hydrophobic interaction and add an electric double-layer repulsion, thus stabilising the suspension.

Various interparticle forces are possible when polymer molecules are present, depending on the polymer concentration and molecular weight, whether or not the polymer adsorbs to the particles, and whether the polymer is charged. Effects of large polymer molecules can be explained as follows: when two surfaces, from which flexible long chains are sticking out into the solution, come close together two effects contribute to the repulsion. In the narrow gap between the surfaces the long chains lose some of their configuration (volume restriction effect). This results in a loss of entropy, in an increase in the free energy and thus in a repulsion. Furthermore the concentration of polymer segments in the gap increases and this so called osmotic effect results in another contribution to the repulsion. This is known as steric stabilisation. But opposite effects can occur at low polymer concentration with high molecular weight polymer where one polymer molecule can adsorb to more than one particle at the same time, causing bridging flocculation. The problem can be overcome by the use of block copolymers, i.e. the stabilising molecule may contain one part that is easily adsorbed (the anchor group) and the other part, the chain, that is easily soluble, e.g. such diblock copolymers as 2-vinyl pyridine-styrene (PVP-PS) and 2-vinyl pyridine-isoprene (PVP-PI) in toluene solution [Watanabe *et al.*, 1992]. More strong effects can arise if polyelectrolytes are used. Adsorption of the polyelectrolytes to neutral particles will give those particles a large charge and thus a effective electrostatic stabilisation mechanism to add to the steric stabilisation: a combination known as electrosteric stabilisation. The charge will be distributed along the adsorbed polymer chains; at low electrolyte concentration the chains repel each other and also other parts of themselves. The examples are ammonium polyacrylate or poly(meth)acrylate and polyacrylic acid or poly(meth)acrylic acid commonly used in aqueous solutions [Hirata *et al.*, 1992; Cesarano III & Aksay, 1988, Pearce, *et al.*, 1995].

3.3.2.4. Dispersion and consolidation of ceramic suspensions

In aqueous solution, probably the most important parameter controlling the stability of dispersion (or hydrosol) is the solution pH. However, electrostatic stabilisation with pH adjustment was reported as being less effective than electrosteric stabilisation with large molecules for ferroelectric powder suspensions. For example, Hirata and Ozaki [1992] reported that high dispersions should be expected at high pH due to electrostatic stabilisation of negatively charged $BaTi_{1-x}Zr_xO_3$ particles since their isoelectric point was pH3.6 to 3.7. But phase separation to dilute aqueous solution and sedimented powder cake occurred within 1 hour in most of the suspensions (5 vol.% solids) at pH3 to 9. This result may be caused by spontaneous formation of a particle network structure by polarisation of ferroelectric particles, indicating difficulty of electrostatic stabilisation of ferroelectric powders. However, no phase separation was observed in the aqueous suspension with polyacrylic ammonium (PAA, average molecular weight 10000) adsorbed powders. Thus, electrosteric stabilisation with PAA was effective to disperse nanometer-sized ferroelectric powders and to increase the solid content of the suspension.

Another problem with the pH adjustment in aqueous solution is the unstability of some ferroelectric ceramic powders in certain pH ranges. For example, though the PZT suspension could be well dispersed at pH below 7, using a polyelectrolyte to stabilise a PZT aqueous suspension is preferred because a large number of the lead ions are dissolved in the acidic condition, which affects not only the sintering behaviour but also the electrical properties of the resultant ceramic [Wen *et al.*, 1991]. A similar result was reported for barium titanate aqueous suspensions where an excessively large solubility and the release of barium ions under acidic condition was found [Lopez *et al.*, 1996]. Therefore, a polyelectrolytes are more favourable for the dispersion of ferroelectric ceramic powders in an aqueous media. Otherwise, ferroelectric ceramic powders are preferably dispersed in a non-aqueous media.

Polymers or polyelectrolytes which adsorb at the particle surface and generate a repulsive interaction caused by the overlap of ion clouds outside of a charged surface (electrostatic stabilisation) or the overlap of absorbed polymer layers (steric stabilisation), will occupy a volume, thus preventing particles from coming into close contact during compaction, and potentially lowering the packing density. This effect will become much more significant when the powder is in the nanometre-sized range [Bergstrom and Shinozaki, 1995]. A compromise has to be made between the range of repulsion and the occupied volume of the dispersant. The optimal situation will be if the polymers or polyelectrolytes could be tailored to be sufficiently thick to prevent agglomeration, hence minimising the occupied volume. However, packing densities as high as those produced from stable suspensions can be obtained by the use of certain additives producing weakly flocculated suspensions [Bergstrom *et al.*, 1992; Chang *et al.*, 1991] rather than well-dispersed suspensions with long-range repulsion. Velamakanmi *et al.* [1990] reported that a simple method for increasing the viscosity of a dispersed alumina suspension over four orders of magnitude was through weak aggregation with certain indifferent electrolytes containing hydrolyzable anions, e.g. NH_4Cl. The slurry with sufficiently high viscosity can prevent mass segregation due to sedimentation. The particles in the viscous slurry, which are covered with short-range repulsive hydration layers, can be packed to a high density during pressure consolidation by apparent lubrication-assisted particle rearrangement. It has been suggested that the addition of a high concentration of different electrolytes to a dispersed ceramic slurry modifies the interaction potential so that the short-range adhesive attraction is diminished by additional repulsive forces. This lower attractive force is still high enough to cause coagulation which raises the viscosity, but small enough to allow easy particle rearrangement during filtration or centrifugation [Chang *et al.*, 1991]. However, it is necessary to optimise the degree of flocculation since a strongly flocculated suspension will lead to low a packing density and an inhomogeneous green body microstructure.

Once a homogeneous slurry has been formed, consolidation, which requires a further increase of the solid loading before final densification to form the ceramic, can be achieved in different ways. One way is to remove some of the liquid from the suspension (drained system). Slip casting, centrifugal casting and pressure filtration are typical drained green shape-forming techniques; the setting mechanism depends on water removal. Thus soluble species tend to migrate and distribute non-uniformly in the formed green body. Porous moulds are used which must be dried carefully before re-utilisation. Furthermore the forming process is generally slow and density gradients may develop within the green body. Another way to consolidate the suspension is to alter the solution conditions of the suspending liquid so that the interparticle forces change from repulsive to attractive (undrained system). Gel casting [Omatete *et al.*, 1991] and direct coagulation casting [Graule *et al.*, 1995a] are two examples of undrained shape-forming techniques based on colloidal processing. Both methods require a well-dispersed suspension of high concentration with reasonably low viscosity which is transferred into the mould. The setting mechanisms depend either on crosslinking of the monomer to form three-dimensional polymer network or on the minimisation of the repulsive double-layer forces to create a strong interparticle forces, e.g. by shifting the pH of a suspension towards the IEP via internal activated decomposition reactions or enzyme catalysed reactions [Graule *et al.*, 1995b], or by creating a salt, thereby increasing the ionic strength of the suspension and compressing the Stern double-layer [Graule *et al.*, 1995c].

3.4. Processing of PZT Films

Although renewed interest in ferroelectric films has existed since the mid-1970's, it has significantly increased during the early 1990's for two principal reasons. First, the techniques and equipment for producing high-quality films are more advanced than in the previous years. Second, the need for such films has become more acute as the trend toward miniaturisation and integration continues. In addition, owing to breakthroughs in the fabrication of thin films of PZT materials, research in this field has gathered greater momentum. The advantages which ferroelectric thin and thick films offer in comparison to bulk materials include: (1) lower voltage operation with thinner structures, (2) higher speed/less power with smaller areas and greater integration, (3) multi-layer/planar structures for simplicity of processing, (4) lower cost with fewer processing steps at lower temperatures, (5) larger areas possible with a minimal cost penalty, (6) unique/multifunction structures that are relatively simple to incorporate [Haertling, 1994].

A number of application areas for PZT films have been developed. For example, PZT thin films have been developed extensively for use as high-capacity non-volatile memories (NVMs) and high capacity dynamic random-access memories (DRAMs). Multilayer piezoelectric actuator technology based on PZT thick films has been proved for several high-volume automotive applications, e.g. fuel-injection systems and suspension systems. But commercialisation has been delayed by the difficulties in meeting performance and reliability requirements at acceptable cost. Despite the difficulties in achieving necessary cost reductions for high-volume production, piezoelectric PZT ceramics continue to find new applications in low-volume, specialised areas where the relatively high costs can be tolerated. Examples include position heads for magnetic recording, scanning tunnelling microscopes, and toner sensors for laser printers [Swartz, 1997]. The primary technical issue to be addressed is the fabrication of relatively thick PZT films, so that sufficiently large piezoelectric stains can be exploited.

3.4.1. PZT Thin Film Processing Techniques

A variety of techniques are available today for the fabrication of PZT thin films. In general, they can be divided into two major categories: i.e. dry and wet processes (Table 3.4). The dry process includes physical vapour deposition (PVD) and chemical vapour deposition (CVD). The wet process includes chemical solvent deposition and chemical melt deposition.

Table 3.4. Thin film deposition techniques

Dry Process	Wet Process
1. Physical Vapour Deposition (PVD)	1. Chemical Solvent Deposition
A. sputtering; B. evaporation (E-beam, resistance, molecular-beam epitaxy)	A. sol-gel; B. MOD (metallo-organic deposition); C. electrochemical reaction; D. hydrothermal growth.
2. Chemical Vapour Deposition (CVD)	2. Chemical Melt Deposition
A. MOCVD (metallo-organic CVD); B. PECVD (plasma enhanced CVD); C. LPCVD (low pressure CVD)	A. LPE (liquid phase epitaxy)

3.4.1.1. Dry process

Generally, the PVD techniques requires a high vacuum, usually better than 10^{-5} torr, in order to obtain a sufficient flux of atoms or ions capable of depositing onto a substrate. The advantages of the PVD techniques are: (1) high purity and cleanliness, (2) compatibility with semiconductor integrated circuit processing, and (3) epitaxial/single crystal film growth is possible. However, these are offset by disadvantages such as (1) slow deposition rates, (2) difficult stoichiometry control in multi-component systems where evaporation or sputtering rates differ considerably, (3) high temperature post deposition anneal is often required for crystallisation, and (4) high capital equipment acquisition and maintenance costs are required. Sputtering and evaporation are examples of well-established and successful PVD techniques. Ion-beam assisted evaporation and sputtering are continuing to become more popular in order to increase film uniformity and deposition rates. Laser ablation, a technique which is similar in concept to low energy thermal evaporation, seems to be more advantageous, for example, it allows congruent transfer of target material, with high deposition rate and lower processing temperature.

The CVD techniques are usually characterised by (1) higher deposition rates, (2) good stoichiometry control, (3) large area, pin-hole free films, and (4) lower initial equipment costs. However, the limited availability and toxicity of some of the precursors for the ferroelectric compositions has posed a real problem for this method.

3.4.1.2. Wet process

Combining the advantages of excellent composition control, spin-on/spray-on/dip-coating capability, low deposition/pyrolysis temperatures and very low equipment costs, the wet chemical techniques, e.g. sol-gel and metallo-organic decomposition (MOD), have already been quite successful and considered the most promising techniques for producing ferroelectric thin films. The sol-gel method involves the preparation of a sol with polymerizable oligomer species which polymerise during spin- or dip-coating deposition. The formation of such networks can be very important for microstructure and crystalline phase development when the films are heat-treated to obtain the crystalline ceramics. The MOD method is a similar technique as sol-gel. It involves the synthesis of a solution containing high molecular weight precursors such as carboxylates which are deposited onto the substrate for further heat treatment causing densification and crystallisation. The difference is that the solution does not form complexes or networks.

The common limitations for the wet chemical techniques are, for example, that film cracking occurs during the drying/firing process because the loss of volatile organic tends to lead to film shrinkage, and further heat treatment is normally required to obtain the desired crystal structure.

3.4.2. PZT Thick Film Processing Techniques

The film deposition techniques discussed above are mostly for the preparation of thin films with thickness less than 5 μm. Preparation of thick films in the range of 5-50 μm is a problem with regard to materials processing. Even lapping or sawing bulk ceramics to thickness less than 50 μm is difficult under any circumstance. PVD and CVD of oxide thick films have often been regarded too expensive, slow and difficult. The more recent technology of sol-gel and MOD is similar in cost to that of conventional doctor blade method, but the typical thickness per coating for wet chemical technique is only about 100 nm. For example, thick PLZT films with sintered thickness of 8 μm need as many as 150 layers deposition [Haertling, 1994]. Theoretical investigation indicates that there will be two instability problems that occur during processing of films from wet chemical techniques [Lange, 1992]: (1) a mechanical instability associated with cracking that occurs, generally, before the film is pyrolysed, and (2) a microstructure instability associated with grain growth in dense polycrystalline films regardless of how they were initially deposited. The film cracking problem will arise because the sequential decrease in film volume during liquid removal, pyrolysis and densification is biaxially constrained by the substrate. Guppy and Atkison [1992] showed that the critical film thickness to avoid cracking problem is about 500 nm for sol-gel derived barium titanate films. By proper modification of using crosslinking agent in the precursor solution, thicker films up to 2 μm have been reported [Yi & Sayer, 1991]. More recently, PZT thick films up to 10 μm can be fabricated via a modification of sol-gel processing [Chen *et al.*, 1996]. Though recent technology also shows that thicker, crack-free films can be fabricated by the multiple recoating of previously pyrolysed thin films via computer-controlled, automatic processing, depositing films to thickness greater than a few microns is not only arduous and time-consuming but results in an increased risk of processing faults (e.g. possible inhomogeneity at the interface between each of the layers).

Nevertheless, thick films with thickness in the range of 5 to 50 μm remains a fruitful area of research and development because certain phenomena, including dielectric (capacitors), electromechanical (piezoelectrics), pyroelectric and electrooptical (optoelectrics) effects can be utilised profitably in materials and devices within this thickness range. For example, multilayer components, such as multilayer actuators, the most frequently used forms of ferroelectric ceramics in the marketplace nowadays, normally consist of layers of one or more ceramic compositions, of thickness in the range of 5 to 500 μm, separated by metallic layers acting as electrodes.

Currently, however, there are no inexpensive thick film fabrication methods available that provide the required quality. A variety of approaches have been investigated to prepare PZT thick films. Hydrothermal process has been directly applied to fabricate PZT thick films from solution but it is difficult to get stoichiometeric PZT compositions because of the large difference between the solubility of each of the components and the unique nucleation and growth mechanism [Obha *et al.*, 1995]. Plasma spraying technology has been used to deposit PZT thick films but it was found that it suffered from the problem of the incongruent melting of the PZT during deposition [Haessler *et al.*, 1995]. Therefore, thick-film technologies mostly rely on the densification of powder films instead of deposition with regard to their costs and properties. The powder layer is formed on the substrate as a powder slurry by, e.g. tape casting [Nieto *et al.*, 1996], screen printing [Zhang *et al.*, 1994] and jet printing [Adachi *et al.*, 1997]. As the liquid phase is removed by evaporation, capillary pressure exerted on the particle network causes the particles to rearrange and increase their pack density. However, sintering was found to be a major problem due to the large ratio of surface to film thickness and relatively high sintering temperatures required. On one hand, large lead loss occurred owing to the large surface area and the evaporation of PbO at temperatures above 800°C. On the other hand, an increase of the sintering temperature was necessary to get the dense PZT film because the lateral shrinkage of the green film applied on a substrate was suppressed [Seffner & Gesemann, 1994]. To reduce the sintering temperature, melt processing was used to fabricate PZT thick films by combining PZT ceramic powders with some low melting crystalline or glass phases (e.g. $Pb_5Ge_3O_{11}$ or $Pb_5(Ge_{1-x}Si_x)_3O_{11}$) to allow the densification at lower temperatures [Collier *et al.*, 1994].

Another possible solution to lower the sintering temperature is to use submicron or nanometre sized PZT powders to make PZT thick films via colloidal processing. Electrophoretic deposition (EPD) is an example of colloidal processing wherein green films are shaped directly from a stable colloid suspension by a DC electric field which causes the charged particles to move toward, and deposit on, the oppositely charged electrode. EPD technique is a combination of two processes: electrophoresis and deposition. Electrophoresis is the motion of charged particles in a suspension under the influence of an electric field. Deposition is the coagulation of particles to a dense mass [Sarkar & Nicholson, 1996]. This technique has been used to make ceramic films and coatings both in aqueous and in nonaqueous suspension. A lot of work has been done on barium titanate thick films [Okamura *et al.*, 1993; Nagai *et al.*, 1993] with thickness from 10 to 100 μm. But few studies have been made in regard to PZT thick films [Sugiyama *et al.*, 1991].