Chapter 2

**Literature Survey of PLZT Ceramics**

2.1 Introduction

La-modified PZT (i.e. PLZT) is a system which has wide spread applications in electronics and electrooptoics [1,2]. PZT and/or modified PZT have extensively been studied in the past using various advanced experimental techniques. Though a large amount of work has been reported on PLZT [3,4,5], with Zr/Ti ratio 65/35, practically no work was done on 52/48 ratio (morphotropic phase boundary ratio) and hence few reported in the literature.

Substitution of Lanthanum for Lead (PLZT) in PZT ceramics changes their macroscopic properties from normal ferroelectric to relaxor ferroelectric types; relaxation phenomenon affects deeply PLZT properties (anomalies). In particular, high values of dielectric permittivity and electromechanical and electro optic coefficients are recorded, which make these materials suitable for various applications such as capacitors, optoelectronic modulators[6-8].

PLZT ceramics with compositions near the morphotropic boundary phase however have been prepared and their structural and dielectric properties investigated[9]. Addition of La seems to enhance crystallization of the raw powders and moves the structural phase towards tetragonal one. Moreover, no secondary phase has been detected. Dielectric measurements revealed the existence of two anomalies at relatively high temperatures $T\approx180$ °C and $T\approx260$ °C. The former, which presence is consistent with a previous work, is interpreted as the temperature at which the transition from ferroelectric-rhombohedral phase to ferroelectric-quadratic phase occurs. The existence of these two anomalies seems to be
dependent on the method of preparation of the samples. Relaxation occurs in our samples at about $y = 0.10$, and the dielectric constant reaches its maximum for $y \approx 0.12$, which value is different from other studies where this maximum occurs at low values of $y$. In the vicinity of the (diffuse) phase transition from ferroelectric to paraelectric phase, the dielectric constant follows a quadratic law in temperature in the case of relaxor behavior and the broadening of the phase transition is shown to increase with La content.

Ever since transparent PLZT was prepared by hotpressing method by Haertling and Land in 1969[10], there was a flurry of activity in preparation of the kind of ceramics using different methods.

The composition was Pb0.92La0.08(Zr0.65Ti0.35)0.98O3 or simply PLZT 8/65/35. The incorporation of aliovalent lanthanum into the lattice enhanced the densification rates of the PZT ceramic bodies, leading to pore-free homogeneous microstructures. In 1971, a detailed work on the preparation and characterization of PLZT transparent ceramics, obtained by conventional mixed oxides technique and hot-pressing densification stage, was published. Only one year later, Haertling and Land reported a novel powder processing of PLZT by chemical routes[11]. This process was based on co-precipitation of alkoxides in presence of PbO and proportioned high chemical and optical uniformity of the hot-pressed PLZT slugs, which started to be produced in commercial scale. Up to that date, many researchers had reported routes to obtain transparent ferroelectric ceramics (TFC) with better characterization and cost benefits, resulting in a list of different processing techniques and hundreds of compositions (most of them with lead and lanthanum elements). The different methods according to relevance is mentioned in the following paragraphs.
2.2 PLZT Ceramics by sintering processes.

Constituent oxides and carbonates in a ceramic when mixed in stoichiometric proportions and calcined at elevated temperatures can give rise to ceramic powders. After being shaped into a desired shape, the agglomerated powder body is fired at a high temperature (less than the melting temperature). Accelerated diffusion of the constituent atoms on the fine particle surfaces due to the surface energy (surface tension) promotes crystal bonding at the contact interface between the two adjacent particles and provides sufficient mechanical strength to the ceramic without significant distortion from the initial molded shape. This firing process is called "sintering," which primarily eliminates pores and increases the ceramic density (see Fig. 2.1). Notice that the physical properties of the sintered body depend not only on the property of each fine crystalline particle, but also on the grain boundary and the pores. An example is found in the mechanical strength: mechanical fracture in ceramic bodies occasionally occurs at the grain boundary (intergranular type). On the contrary, when the crystal itself has a strong cleavage character, the polycrystalline material shows higher mechanical strength. During sintering, the grains grow and the grain shape also changes significantly. However, it is well recognized that the raw powder characteristics strongly affect the manufacturing conditions and the final product characteristics. In general, the sintering is accelerated with decreasing particle size of the raw powder (i.e., with increased specific surface area), because the driving force of sintering is related to the surface energy of the particles. Moreover, for fine powders, the necessary diffusion length of the atoms for sintering becomes shorter, which accelerates pore diffusion. This results in high density ceramics.
Pore-free PLZT can be obtained by sintering under atmospheric pressure in oxygen or by applying a vacuum during the early stages of sintering. It is more usual to prepare cylindrical blocks of material by hot-pressing in Si3N4 or SiC dies as shown in Fig. 2.2. 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. PLZT ceramic with a grain size less than 5 µm can be obtained by hot-pressing at 1200°C and 40MPa and holding for about 6 h. The crystals can be increased in size by a subsequent anneal in an atmosphere containing PbO vapour. Plates of large area for wide aperture devices require very careful annealing in order to eliminate variations in birefringence due to minor variations in density without undue crystal growth. Plates of the required thickness are cut from the hotpressed pieces and the major
surfaces are lapped and polished. If the plates are to be used exploiting a longitudinal electro-optic effect, where the electric field and light are parallel, transparent electrodes of indium tin oxide (ITO) can be applied to the major surfaces by sputtering and coated with blooming layers to reduce the loss of light by reflection. Where the field is to be at right angles to the direction of light propagation, grooves can be formed in the major surfaces and gold deposited in them to form an interdigitated electrode system. Blooming layers are again essential because the refractive indices may be about 2.5, so that approximately 40% of normally incident light would otherwise be reflected.

Figure. 2.2 Apparatus for hot-pressing PLZT[12].
2.3 Hydrothermal Processes

Hydrothermal synthesis is one of the most important tools for advanced material processing at low temperature (Byrappa and Adschiri[13] 2007). It was used for preparing PZT powders (Deng[14] et al 2003; Piticescua[15] et al 2004; Wang[16] et al 2004; Dunn [17]2008), films(Euphrasie [18]et al 2003;Ahn[19]et al 2006; Ko[20] et al 2007)and even nanowhiskers(Yang[21] et al 2007) from different precursor feedstocks. The desirable products can be synthesized by controlling the experimental parameters such as alkalinity, reagent, mineralizer, hydrothermal treatment temperature and time. In the open literature of PLZT and PZT synthesis, the undesirable products such as Pb2Ti2O6 (Wang et al 2004), PbO and TiO2 (Deng et al 2003; Dunn 2008) accompanied in the powders. These would depress the PLZT or PZT properties.

The procedure of preparation of the samples can be conducted in two-steps. In the first step, aqueous solutions of ZrOCl2, 8H2O 0.1M and TiOCl2-xHCL (Ti: 15%) are mixed, with stirring, and 2M KOH has to be added until precipitation to obtain a precipitate (ZTO) which should be then washed with distilled water for several times to obtain its neutrality. ZTO has to be put into an aqueous solution of 0.2M lead acetate and 0.5M lanthanum acetate. Thereafter, the solution obtained, whose pH has to be raised to 11 by adding 2M KOH, and then put into an autoclave ( Filling ratio superior to 80%) and heated at 200 °C during 12 hours. The resultant PLZT suspension must be filtered and the remaining product,washed with distilled water for several times and finally dried at 70 °C in an oven. Annealing of the powders, at different temperatures, must be done in air.
2.4 Co-Precipitation Technique

The coprecipitation method has been employed to realize enhanced homogeneity. Adding a precipitant into the liquid solution of mixed metal salts produces a homogeneous precipitate. Thermal dissolution makes homogeneous powders from the precipitate. For example, BaTiO(C2H4)2.4H2O with the Ba/Ti ratio exactly equal to 1:1, on an atomic scale, can be precipitated from an aqueous solution of BaCl2 and TiCl4 by dripping in oxalic acid. Thermal dissolution of this precipitate provides fine stoichiometric BaTiO3 powders with good sintering characteristics. For PLZT, Pb(NO3)2, La(NO3)3.6H2O, ZrO(NO3)2.2H2O and TiO(NO3)2 are used as the starting materials.[22] First, the water solutions of each nitrate are mixed in the desired proportion, then a half volume of ethanol is added. Oxalic acid diluted with ethanol is dripped slowly into the nitric solution, leading to the precipitation of the PLZT oxalate. Thermal dissolution is carried out at 800°C. In the above coprecipitation methods, thermal dissolution of the precipitate is finally required to obtain the desired powder. However, the oxide powder can be obtained directly through the precipitation process in special cases. A direct precipitation method for BaTiO3 is introduced here. By dripping Ti(OR)4 (R: propyl) into Ba(OH)2 water solution, fine high-purity stoichiometric BT powders with an average particle size of 10 nm can be obtained directly.

Takasu et al. studied the effects of grain size on PLZT.[23] They obtained PLZT (9/65/35) powders by coprecipitation. Various grain sizes were prepared by hotpressing and by changing sintering periods. PLZT (9/65/35) shows significant dielectric relaxation (frequency dependence of the permittivity) below the Curie point of about 80oC, and the dielectric constant tends to be higher at lower frequency. For grain size larger than 1.7 µm, the dielectric constant decreases with decreasing grain size. Below 1.7 µm, the dielectric constant increases rapidly. As the grain size becomes smaller, the maximum strain decreases monotonically.
However, when the grain size becomes less than 1.7 µm, the hysteresis is reduced. This behavior can be explained as follows: with decreasing grain size, (anti)ferroelectric (ferroelastic) domain walls become difficult to form in the grain, and the domain rotation contribution to the strain becomes smaller (multidomain - monodomain transition model). The critical size is about 1.7 µm. However, note that the domain size is not constant, but is dependent on the grain size, and that in general the domain size decreases with decreasing grain size.

2.5 Sol Gel (Alkoxide Hydrolysis) Technique

When metal alkoxides M(OR)n (M: metal atom, R: alkyl) are mixed in alcohol in an appropriate proportion, and water is added, the hydrolytic reaction produces alcohol and the metal oxide or metal hydrate. This is sometimes called the sol-gel method. The alkoxide method can produce very fine and very high purity powders. Since metal alkoxides are evaporative, purification is easily accomplished through distillation. Also high purity can be sustained during the hydrolytic reaction because no other ion doping is necessary. The mechanisms of hydrolysis and condensation can be summarized as follows:

(a) Hydrolysis \[ H - O + M - OR \rightarrow H - O - M + ROH \]

| H |

(b) Alkoxylation (Removal of H as an alcohol)

\[ M - O + M - OR \rightarrow M - O - M + ROH \]

| H |
(c) Oxolation (Removal of H as water)

$$\text{M} - \text{O} + \text{M} - \text{OH} \rightarrow \text{M} - \text{O} - \text{M} + \text{OH}_2$$

In order to obtain BT powders, Ba(OC\text{3H7})_2 and Ti(OC\text{5H11})_4 are diluted with isopropyl alcohol(or benzene). Choosing an appropriate hydrolysis condition (pH), very fine stoichiometric BT powders with good crystallinity and a particle size of 10 - 100 Å can be obtained (agglomerate size = 1 µm). Also the hydrolytic process gives a specimen powder with purity more than 99.98%, leading to a remarkable increase in the permittivity of the sintered ceramic in comparison with samples prepared by oxide-mixing.[24] In the case of PZT preparation, Pb alkoxide is relatively difficult to obtain compared to Ti and Zr alkoxides. Thus, one way is to employ a two-stage method for convenience: (Zr,Ti)O_2 is prepared by the alkoxide method, and PbO is added later for use in the solid state reaction.[25] A partial sol-gel method combined with inexpensive ready-made nanosize powders will be a promising direction to achieve reduction in production costs. Of course, the other way is to use Pb alkoxide; zirconium n-butoxide Zr[O(CH2)3CH3]4 and titanium isopropanoxide Ti[OCH(CH3)2]4 are added into lead acetyl acetonate Pb(CH3COCHCOCH3) to obtain PZT precursor.

### 2.6 Characterisation of PLZT

When transparent Lead Lanthanum Zirconate Titanate (PLZT) ferroelectric materials were first developed, ferroelectric ceramics have been thoroughly researched, and their characteristics studied to the point that they have now taken
their place alongside single crystals as legitimate candidates for certain electrooptic applications. The electrooptic properties of PLZT materials are intimately related to their ferroelectric properties. Consequently, varying the ferroelectric polarization with an electric field, such as in hysteresis loop, also produces a change in the optical properties of the ceramics. [26]. Applications of ferroelectric materials in a film form are growing due to the need for miniaturization and integration of electronic components, and due to development of microtechnologies, material fabrication and engineering. Aside from the obvious advantages, such as smaller size, less weight and easier integration to integrated circuit technology, ferroelectric films offer additional benefits, including lower operating voltage, higher speed, and the ability to fabricate unique micro-level structures. In addition, the sintering temperatures of the films are usually hundreds of degrees Celsius lower than that of the bulk, and this often can be the deciding factor in a successful design and applications [27-30]. Among the most common ferroelectric film applications are non-volatile memories, integrated optics, electrooptical displays, microactuators, microtransducers, and capacitors fabricated in a film form.

2.6.1 Dielectric Phenomenon in PLZT ceramics

Lanthanum substitution for Lead (PLZT) in these materials changes their macroscopic properties from normal ferroelectric to relaxor ferroelectric types; relaxation phenomenon affects deeply PLZT properties (anomalies). In particular, high values of dielectric permittivity and electromechanical and electro optic coefficients are recorded, which make these materials suitable for various applications such as capacitors,optoelectronic modulators, these anomalies manifest themselves within a broad temperature region around a temperature, Tm corresponding to the maximum in the dielectric permittivity; the phase transition is
called ‘diffuse phase transition’ (DPT). Several models and approaches have been developed to interpret this DPT involving different mechanisms: chemical heterogeneities, superparaelectric behaving due to mesoscopic heterogeneities,\cite{34-38}. However, details concerning the physical process of the DPT remains unclear. As mentioned above, a maximum response of different characteristics, among them the electromechanical coupling coefficient, is obtained due to the coexistence of ferroelectric tetragonal and ferroelectric rhombohedral phases near the MPB. Based on this coexistence, different phase diagrams have been proposed \cite{39,40}. Moreover, this enhancement of the electromechanical response is suggested to be linked with the instability in the vicinity of the rhombohedral to tetragonal transition \cite{41}.

Low temperature dielectric measurements have revealed the presence of two anomalies in the real part of the dielectric constant of PZT materials near the MPB \cite{41}. The occurrence of the anomaly corresponding to the lowest temperature was imputed to a tetragonal to monoclinic phase transition, which was supported by XRD studies of Noheda et al. \cite{42}. The presence of such anomaly has also been reported in dielectric studies of PZT materials near the MPB \cite{43}. With the aim of studying the effect of La addition on the structural and dielectric properties of the morphotropic phase boundary composition Pb(Zr0.52Ti0.48)O3 (PZT), some researchers have prepared, using the hydrothermal process, (Pb1-yLay)(Zr0.52Ti0.48)O3 (PLZTy) powders, with y = 0, 0.015, 0.03, 0.06, 0.08, 0.10, 0.12, and 0.15. Indeed, addition of La (La belongs to the so-called soft-dopants additives) is known to improve permittivity and piezoelectric coupling coefficient of PZT materials \cite{44}. Moreover, hydrothermal processing, contrary to other methods of preparation, in particular the solid-state reaction method, permits a good control of composition and morphology of the powder, does not necessitate
any milling and calcinations operations and has lower agglomeration effects (the latter having dramatic effects on the consolidation and densification behaviour of the powder)\cite{45,46}.

### 2.6.2 SEM Studies

![SEM micrographs](image)

**Figure 2.3.** SEM micrographs of the PLZT x/65/35 ceramics with different content of lanthanum\cite{47}: a) La = 13, b) La = 9.75, c) La = 8.5.

A concise and elaborate study on Lanthanum modification of PZT and its effect on the microstructure is very hard to find in the existing literature. The above photographs (Fig. 2.3) although confirms that grain size of the ceramic increase with increasing amount of La, the result has not been confirmed using SEM micrographs by other workers in the field.

### 2.6.3 Piezoelectricity

The PLZT x/54/46 has been studied by A. Su´arez-G´omez et. al\cite{48} and had shown a pure perovskite phase with coexisting tetragonal (F$_T$) and rombohedral (F$_{R(HT)}$) phases, and the grain size was dramatically reduced with further doping as well as porosity. The Curie temperature was reduced as the long range interactions
were weakened due to the simultaneous A and B sites substitutions with La and Nb, respectively. The PLZTN 10/54/46 showed, in our opinion, the best overall piezoelectric performance and hydrophone like behavior, while the other compositions were affected by their structural features. They also discussed and represented the data on longitudinal piezoelectric coefficient ($d_{33}$) and dielectric constant ($\varepsilon$) of nano PZT ceramics at various lanthanum concentrations. It is seen that the longitudinal piezoelectric coefficient and dielectric constant increases with an increase in lanthanum concentration. But when it comes to $d_{33}$ it is contrary to the existing trend. Since $d_{33}$ is important when the material is used for hydrophone applications.

2.6.4 Pyroelectricity

Santos et.al\cite{49} studied PLZT (10/65/35) produced by conventional mixed oxides method, submitted to the first calcination stage at 1173 K/3 h. The pyroelectric current $I_p$ and the remanent polarization $P_r$ are shown in Fig. 2.4. The $I_p$ peak arises at 249 K, where the remanent polarization presents an inflection point. In fact, at temperatures few degrees above $T_p$ (temperature of the pyroelectric current peak) the remanent polarization reaches values approximately close to zero. This result also agrees with other previously reported for PLZT 10/65/35 ceramics\cite{50}. The sharpness of the pyroelectric current curve clearly indicates the single-phase nature of this sample. Nevertheless, the $I_p$ vs. $T$ curve do not reach zero values until 320 K. This effect may be related to some spurious conductivity, certainly originated from spatial charge building up during the heating.
Some propriety ceramics of lanthanum- modified lead zirconate titanate (PLZT), denoted as STPZT-1 and MnO2 doped PLZT denoted as STPZT-2 including commercially available modified lead zirconate titanate ceramic (BM 740) from Sensor Technology Limited, Canada [51] are reported in the literature. BM 740 has been chosen as it exhibits low frequency drift over normal working temperature and the aging of permittivity is low [51]. This sample is also understood to be a potential candidate for pyroelectric applications. Due to the proprietary reasons the exact cation(s) modified recipe of BM740 remained unknown. It is worthy to mention that these ceramics have been prepared using optimized recipe and proprietary processing technology. Their usefulness in pyroelectric infrared detectors is compared with the results of other candidate pyroelectric materials. The properties and materials’ figures-of-merit of modified lead zirconate ceramics

**Figure 2.4** Pyroelectric current ($I_p$) and remanent polarization ($P_r$) for the PLZT 10/65/35 hot-pressed ceramic
are mentioned in the references [52] through [59] along with the results obtained in the present research for comparison purposes.

2.7 References


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