

## CHAPTER 2

### EXPERIMENTAL

PZT and PLZT powders were first prepared by solid state reaction of the constituent metal oxides or carbonates.<sup>31-33</sup> However such reactions often lead to compositional and structural inhomogeneities in the powders produced. Moreover, ceramics prepared at high temperatures have a very large particle size, higher impurities content due to repetitive calcination and grinding steps, have a lower chemical activity and are not suitable for enhancing the dielectric properties for high performance uses. Precipitation from nitrate solutions<sup>15, 45-47</sup> is one of the chemical processing techniques that can produce fine particle size, a high degree of chemical homogeneity of the powder and reduced calcination temperature of the PZT powder. The hydrothermal synthesis<sup>66-70</sup> is a convenient technique for the preparation of various multicomponent oxide materials, which have utility in numerous electronic applications. Hydrothermal systems are useful for the precipitation of ceramics powder of fine particle size and uniform morphology in a single experimental step at moderate temperature and pressure. The most commonly used precursors for the hydrothermal synthesis of PZT powders are nitrates, chlorides, oxychlorides, acetates, hydroxides and Zr or Ti alkoxides.

The use of catalyst or mineralizer for synthesis of PZT powders is necessary as it increases the solubility of the starting material precursors. Concentrations of the catalyst play an important role in the formation of PZT and PLZT.

The composition ratio of Zr:Ti is around 0.52:0.48 so that the desired composition  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  is close to the morphotropic phase boundary zone in the phase diagram of PZT solid solution.

For PLZT, the ratio of Pb:La:Zr:Ti is 0.88:0.12:0.65:0.35 is the composition for the PLZT with 12 mole %La.

## 2.1 CHEMICALS

1. Lead acetate,  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ , assay 99%, Aldrich, U.S.A.
2. Zirconium-n-propoxide:  $\text{Zr}[\text{O}(\text{CH}_2)_2\text{CH}_3]_4$ , assay 70 % w/w in n-propanol, Fluka, Switzerland
3. Titanium isopropoxide,  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ , assay 97%, Aldrich, U.S.A.
4. Lanthanum acetate,  $\text{La}(\text{CH}_3\text{COO})_3 \cdot 1.5 \text{H}_2\text{O}$ , assay 99.9 %, Aldrich, U.S.A.
5. Ammonia solution,  $\text{NH}_4\text{OH}$ , assay 25 %, BDH, England
6. Potassium hydroxide,  $\text{KOH}$ , assay 85%, Carlo Erba, Italy
7. Sodium hydroxide,  $\text{NaOH}$ , assay 99%, Merck, Germany
8. Isopropanol,  $\text{C}_3\text{H}_8\text{O}$ , assay > 99 %, Merck, Germany
9. Absolute ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , assay 99.0-100.0 %, Merck, Germany
10. Ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , assay 95 %, Merck, Germany

## 2.2 APPARATUS AND INSTRUMENTS

1. Thermogravimetric analyzer (Perkin –Elmer, TGA 7), U.S.A.
2. Differential thermal analyzer, (Shimadzu Thermal Analyzer), Japan
3. X-ray diffractometer (Siemen S, D500), Germany
4. Scanning electron microscope (JEOL JSM 840A), Japan
5. Transmission electron microscope (JEOL JEM 1200 EX II), Japan
6. Grinder-polisher (ECOMET 3), Buchler, Germany
7. Vernier (Zim-ZEEM), China
8. Furnace (SCF 1200, Carbolite), England
9. Furnace (Thermolyne), England
10. Vacuum oven (VOS-300 SD), Japan
11. Balance (Mettler Toledo AB 304-S), England
12. Impedance/Gain-Phase analyzer (HP4194A), U.S.A.
13. Dielectric test fixture (HP 16451B), U.S.A.

## 2.3 EXPERIMENTAL PROCEDURES

### 2.3.1 Preparation of PZT powders

#### Preparation of the stock solution:

The clear solutions of 0.025 M zirconium n-propoxide and 0.025 M titanium isopropoxide in isopropanol were prepared and mixed together into the teflon-line cup. An aqueous solution of 0.025 M lead acetate in deionized water was then added into the mixed solution in the ratio theoretically necessary to obtain the desired  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ . KOH or NaOH at various concentrations were used as the mineralizers for adjusting pH of the final solution.

#### Hydrothermal treatment:

Hydrothermal synthesis of the PZT powders was performed under autogeneous pressure in a 500 ml teflon-line cup autoclave. The synthesis temperature varied from 50 to 200 °C, and the holding periods ranged from 6 to 48 hours. The total volume of the solution should be below 125 ml. The conditions above were producing an autogeneous pressure up to 0.6 MPa in the hydrothermal vessel. After cooling down, the solid portion was separated by filtration. The product was washed successively with deionized water until a neutral pH was reached. The wet powders were dried in an oven at 100 °C for 12 hours. Figure 2.1 shows the flow chart for preparation PZT powders by hydrothermal process.

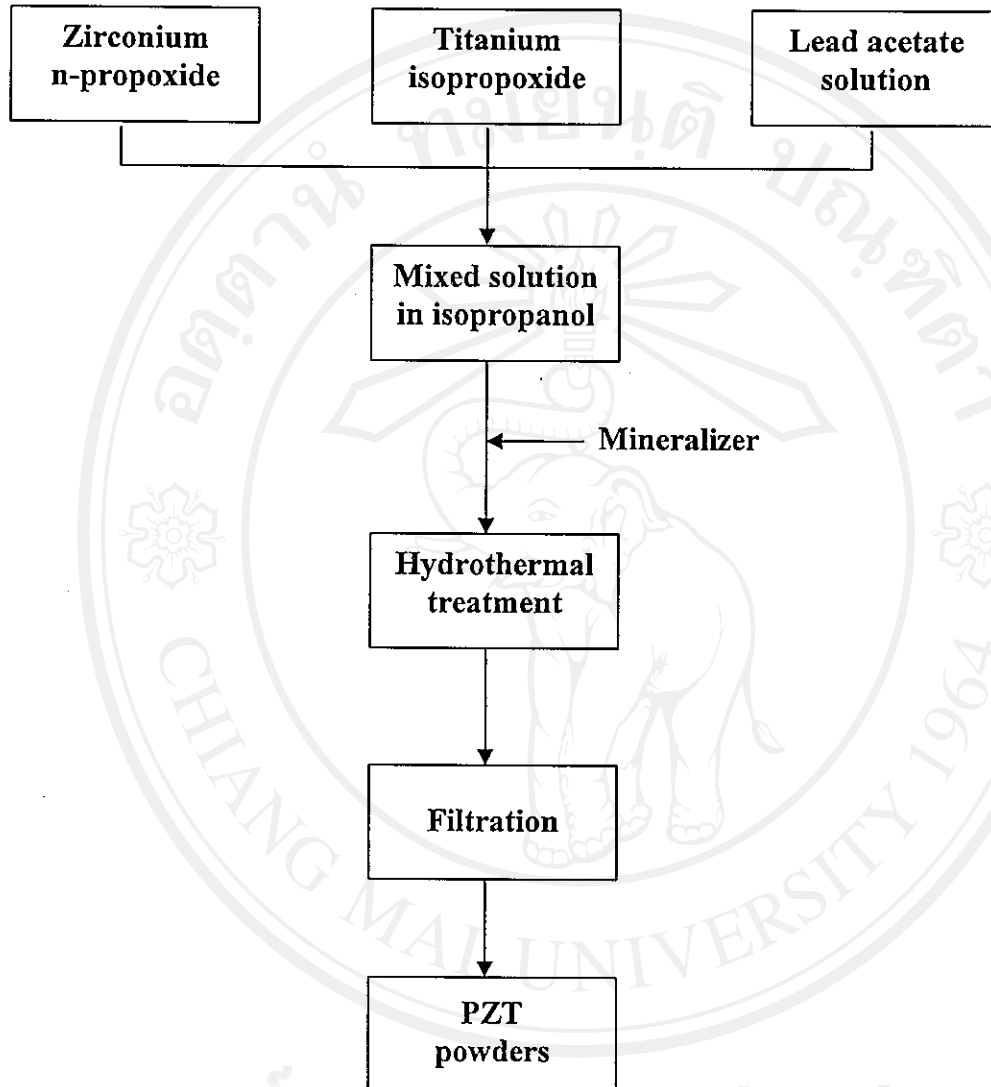


Figure 2.1 Schematic diagram for the preparation of PZT powders by hydrothermal process.

### 2.3.2 Preparation of PLZT powders

The clear solution of 0.025 M zirconium n-propoxide and 0.025 M titanium isopropoxide in isopropanol were mixed in the teflon-line cup. An aqueous mixed solution of 0.025 M lead acetate and 0.025 M lanthanum acetate, at 8, 9, 10 or 12 mole % lanthanum, was added into the zirconium and titanium mixed solution. KOH was used to adjust pH of the final solution. The same procedure used to prepare PZT powders by hydrothermal process was used to synthesize PLZT powders. The synthesis temperature was varied from 50 °C to 200 °C and the holding periods varied from 6 to 24 hours.

## 2.4 POWDERS CHARACTERIZATION

### 2.4.1 Thermal Analysis (TG-DTA)

The thermal analysis of PZT and PLZT powders were studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). These techniques were used to detect the weight loss and endothermic or exothermic changes of the powders.

#### Sample preparation

The heating profile of PZT and PLZT powders were carried out using thermogravimetric analyzer (Perkin-Elmer TGA 7) at a heating rate of 10 °C/min, heated from 100 ° to 850 °C. The curve of weight change versus temperature provides information about thermal stability and composition of the original sample, the intermediate compounds and the residue.

Differential thermal analysis (DTA) is a technique used for investigating the physical or chemical change within the powders. Heat or enthalpy changes, either exothermic or endothermic, were caused by phase transition such as crystalline structure inversions and decomposition reactions. In this technique, the sample temperature was continuously compared with a reference material temperature, the difference in temperature being recorded as a function of furnace temperature or time.



#### 2.4.2 X-ray Diffraction (XRD)

The crystalline structure and phase transformation of PZT and PLZT powders were studied by X-ray diffractometry.

##### Sample preparation

Crystallographic and phase analyses were performed on an X-ray diffractometer (D 500, Siemens) operating at 25 kV and 20 mA, using  $\text{CuK}\alpha$  radiation. The detection range of  $2\theta$  values was  $20^\circ$  to  $60^\circ$  with scan step increments of  $0.1^\circ$ . Identification of crystalline phases was carried out by comparison of XRD patterns with JCPDS standards.

#### 2.4.3 Scanning Electron Microscopy (SEM)

The particle size, morphology and microstructure of PZT and PLZT powders were investigated using scanning electron microscopy.

##### Sample preparation

The particle size, morphology and microstructure of PZT and PLZT powders were characterized by scanning electron microscope (JEOL JSM 840A). The powder samples were dispersed in absolute ethanol using an ultrasonic bath. The suspension was dropped on gold conductive tape that attached to the surface of the SEM brass stub. The stub was then coated with palladium-gold by plasma sputtering for 6 minutes. An accelerating voltage of 5 kV was used.

## 2.5 CERAMICS CHARACTERIZATION

### 2.5.1 Ceramics preparation

PZT and PLZT powders were pressed in a 2 cm cylindrical die, the pressure applied was 3 MPa. The green pellets were placed in an alumina crucible. The specimens were embedded in a PZT bed and also surrounded in PZT powders, which was used for the PbO atmosphere buffer. Sintering was carried out in a furnace under air atmosphere using a heating and cooling rate of 10 °C/min. The sintering temperature was varied from 1000 °C to 1250 °C at difference soaking time of 3 and 5 hours.

### 2.5.2 X-ray Diffraction (XRD)

The phase present after sintering was identified on an X-ray diffractometer (D 500, Siemen) operating at 25 kV and 20 mA, using  $\text{CuK}_\alpha$  radiation. The detection range of  $2\theta$  values was 20° to 60° with scan step increments of 0.1°.

### 2.5.3 Scanning Electron Microscopy (SEM)

The sintered microstructure of PZT and PLZT ceramics were studied by scanning electron microscopy (JEOL JSM 840A).

#### 2.5.4 Measurement of shrinkage

Shrinkage was measured by comparing the size of the green compact and the sintered pellets. The shrinkage percentage can be calculated by:

$$S_d = [1 - (D_i / D_f) ]$$

Where  $S_d$  is percent linear shrinkage,

$D_i$  is the diameter of the green compact,

$D_f$  is the diameter of the sintered sample.

#### 2.5.5 Measurement of density

The density of sintered pellets was measured by an immersion technique and calculated using Archimedes principle. A dry sample was weighed and then submerged in hot distilled water for 2 hours to ensure that all-open porosity within the pellets were filled. The saturated pellets were first weighed in room temperature distilled water and weighed again in the air using a wire basket. Density of the pellets can be calculated by the following formula:

$$\text{Density} = \frac{Wt_{(dry)} D_{(liq)}}{Wt_{(sat)} - Wt_{(susp)}}$$

Where  $Wt_{(dry)}$  is the weight of the dry pellets,

$Wt_{(sat)}$  is the weight of the saturated sample weighing in air,

$Wt_{(susp)}$  is the weight of the sample weighing in distilled water,

$D_{(liq)}$  is the density of the water at the experiment temperature.

### 2.5.6 Measurement of dielectric constant

The dielectric constant of sintered pellets was measured at room temperature using Solartron 1260 Impedance Analyzer and Dielectric Test Fixture (HP 16451B) for their capacitance.

The dielectric constant, or relative permittivity ( $\epsilon_r$ ) was calculated using the following equation:

$$\epsilon_r = \frac{C \cdot t}{A \cdot \epsilon_0}$$

- Where
- $\epsilon_r$  is the relative permittivity of piezoelectric material,
  - $\epsilon_0$  is the relative permittivity of free space ( $8.854 \times 10^{-12}$  F/m),
  - A is the area of the electrodes or area of disc space (m),
  - t is the distance between electrodes or sample thickness(m),
  - C is the measured capacitance at 1 kHz (F)

### 2.5.7 Measurement of impedance spectroscopy

The electrical properties were investigated by impedance spectroscopy. Measurements were performed on 8 mm × 2 mm cylindrical samples. Platinum electrodes were made by spread a platinum paste coating (Demetron 308 A) on the parallel faces which was dried at 900 °C for 60 min. The measurements were carried out with an applied potential of 500 mV in the frequency range from 5 Hz to 13 MHz. A Solartron 1260 Impedance Analyzer controlled by a computer was used. The samples were placed in a sample holder with a two-electrode configuration. The measurements were taken from 25 to 600 °C with a 50 °C step in atmospheric air. After each measurement, an interval of 30 min was used prior to the stabilization of the temperature and properties. No thermal hysteresis was detected during the measurements taken on the heating and cooling cycle. The measured values of impedance  $Z^* = Z' + iZ''$  were analyzed using the software Zview7, adopting equivalent circuits to simulate the immitance spectra and complex diagrams.

The activation energies ( $E_a$ ) were calculated using the following equation:

$$\sigma' = \sigma_0 \exp(-E_a/kT)$$

Where

$\sigma$  = Conductivity

$\sigma_0$  = Pre-exponential factor

$E_a$  = Apparent activation energy for conduction process

$k$  = Boltzmann' constant

$T$  = Absolute temperature (K)