CHAPTER 2

EXPERIMENTAL

PZT and PLZT powders have been first prepared by solid state reaction of the constituent metal oxides or carbonates[31-33]. 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[15, 45-47] 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[66-70] is the 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 the 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 synthesis.

The composition ratio of Zr:Ti is around 0.52:0.48 so that the desired composition $Pb(Zr_{0.52}Ti_{0.48})O_3$ 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 0.91:0.09:0.65:0.35 is the composition for the PLZT with 9 mole %La. The desired compositions are 8, 9, 10 and 12 mole% of lanthanum.

2.1 CHEMICALS

1. Lead nitrate, $Pb(NO_3)_2$, assay 99+ %, Aldrich , U.S.A.
2. Lead acetate, $Pb(CH_3COO)_2$. $3H_2O$, assay 99%, Aldrich, U.S.A.
3. Zirconium-n-propoxide: $Zr[O(CH_2)_2CH_3]_4$, assay 70 % w/w in n-propanol, Fluka, Switzerland
4. Titanium isopropoxide, $Ti(OC_3H_7)_4$, assay 97%, Aldrich, U.S.A.
5. Lanthanum nitrate, $La(NO_3)_3$. $3H_2O$, assay 99.9%, Aldrich, U.S.A.
6. Lanthanum acetate, $La(CH_3COO)_3$. 1.5 H_2O, assay 99.9 %, Aldrich, U.S.A.
7. Ammonia solution, NH_4OH, assay 25 %, BDH, England
8. Nitric acid, HNO_3, assay 65 %, Merck, Germany
9. Hydrogen peroxide, H_2O_2, assay 30 %, Carlo Erba, Italy
10. Potassium hydroxide, KOH, assay 85%, Carlo Erba, Italy
11. Sodium hydroxide, NaOH, assay 99%, Merck, Germany
12. Isopropanol, C_3H_8O, assay > 99 %, Merck, Germany
13. Sulphuric acid, H_2SO_4, assay 98%, Carlo Erba, Italy
14. Ammonium acetate, CH_3COONH_4, assay 97%, Fluka, Switzerland
15. Potassium chromate, K_2CrO_4, assay 97%, Merck, Germany
16. Phosphoric acid, H_3PO_4, assay 85%, Carlo Erba, Italy
17. Cupferron, $C_6H_5N(NO)ONH_4$, assay 97 %, Aldrich, U.S.A.
18. Absolute ethanol, C_2H_5OH, assay 99.0-100.0 %, Merck, Germany
19. Ethanol, C_2H_5OH, assay 95 %, Merck, Germany
20. Ammonium sulphate, $(NH_4)_2SO_4$, assay 99%, Carlo Erba, Italy

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 (Crystal Structure Limited (SCL), D5000), England
4. Scanning electron microscope (JEOL JSM 840A), Japan
5. Transmission electron microscope (JEOL JEM 1200 EX II), Japan
6. Atomic absorption spectrophotometer (Shimadzu (AA 680)), Japan
7. Grinder-polisher (ECOMET 3), Buchler, Germany
8. Vernier (Zim-ZEEM), China
9. Freeze-dryer (FTS systems), U.S.A.
10. Furnace (SCF 1200, Carbolite), England
11. Furnace (Thermolyne), England
12. Vacuum oven (VOS-300 SD), Japan
13. Balance (Mettler Toledo AB 304-S), England
14. Particle size analyzer, (Malvern Masterizer), England
15. Impedance/Gain-Phase analyzer (HP4194A), U.S.A.
16. Dielectric test fixture (HP 16451B), U.S.A.

2.3 EXPERIMENTAL PROCEDURES

2.3.1 Preparation of PZT powders

2.3.1.1 Coprecipiation from nitrate solutions

Preparation of titanium precursor solution:

Titanium isopropoxide was hydrolyzed by ammonia solution to form white, solid titanic acid, $Ti(OH)_4$. This white solid was dissolved in dilute nitric acid under continuous stirring at temperature below 10 °C to ensure that all $Ti(OH)_4$ was changed into $TiO(NO_3)_2$ solution. Hydrogen peroxide was added to this solution to form the stable reddish brown titanium peroxo-complex. Color of final solution was reddish brown.

Preparation of zirconium precursor solution:

The same procedure used to prepare the titanium precursor solution was used to prepare the zirconium precursor solution. Zirconium n-propoxide was hydrolyzed by ammonium hydroxide and dissolved in dilute nitric acid. After a few drop of hydrogen peroxide, the final solution showed a clear light yellow color.

Preparation of PZT powder:

The flow chart of the preparation of PZT powders which modified from the preparation of PLZT by Thomson[15] is shown in Figure 2.1. The 0.025 M titanium and 0.025 M zirconium precursor solutions were mixed. An aqueous solution of 0.025 M lead nitrate in deionized water was then added to the mixed solution in the ratio theoretically required to obtain the desired $Pb(Zr_{0.52}Ti_{0.48})O_3$ composition. The mixed solution was heated to 75 °C. Ammonia solution was then added to adjust the pH of the solution to be neutral. After that the solid portion was separated from the solution

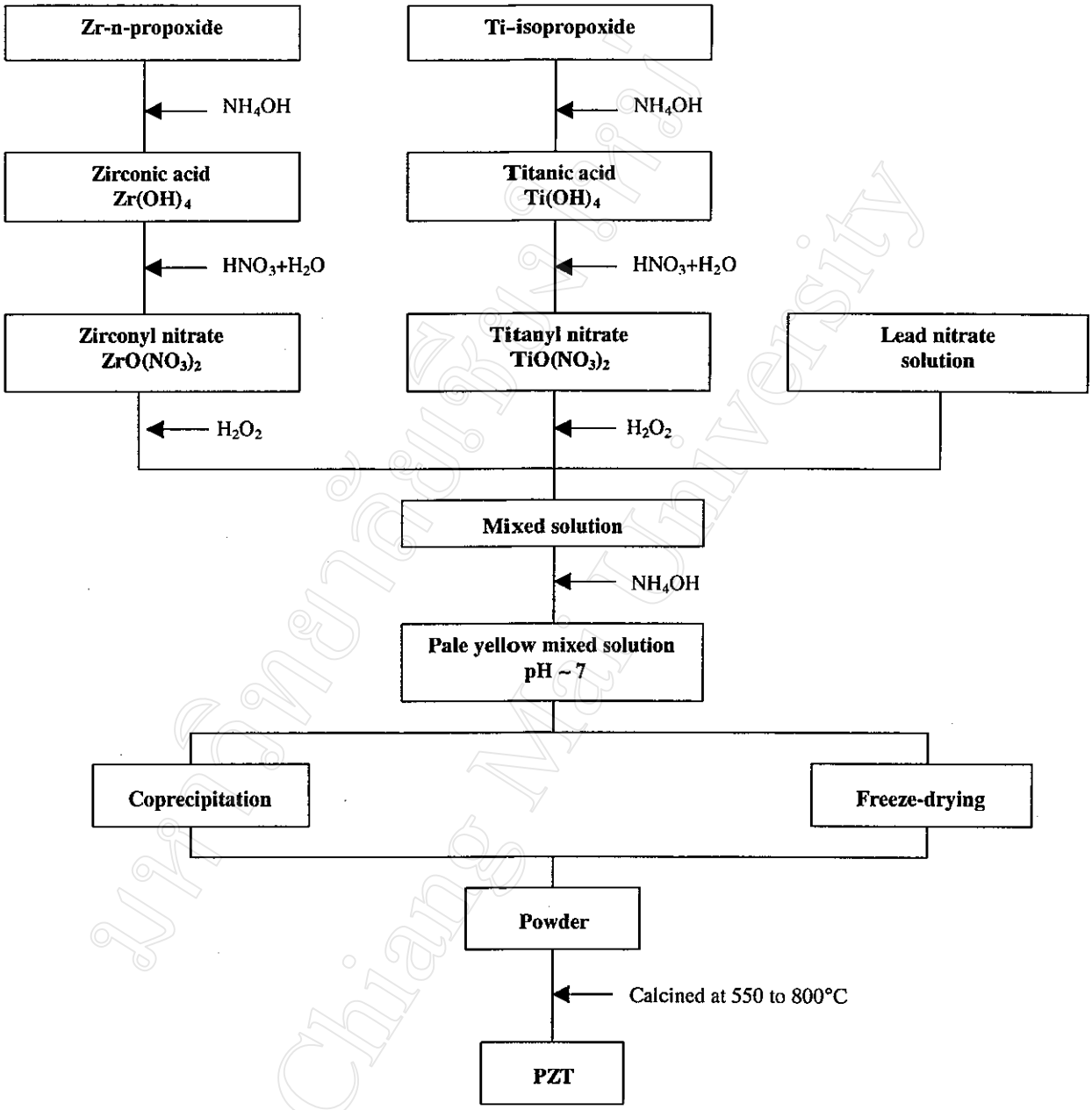

Figure 2.1 Schematic diagram for the preparation of lead zirconate titanate powders.

using two different methods, either by freeze-drying or by precipitating with ammonia solution. The solid portions obtained by both techniques were dried at 100 °C and calcined at 550 to 800 °C.

2.3.1.2 Hydrothermal process

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 $Pb(Zr_{0.52}Ti_{0.48})O_3$, 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 time ranged from 6 to 48 hours. The total volume of the solution should be below 125 ml, which producing an autogeneous pressure up to 0.6 MPa. After cooling down, the solid portion was separated from the extracted suspensions by filtration. The product was washed successively with deionized water until neutral pH. The wet powders were dried in an oven at 100 °C for 12 hours. Figure 2.2 shows the flow chart for preparation PZT powders by hydrothermal process.

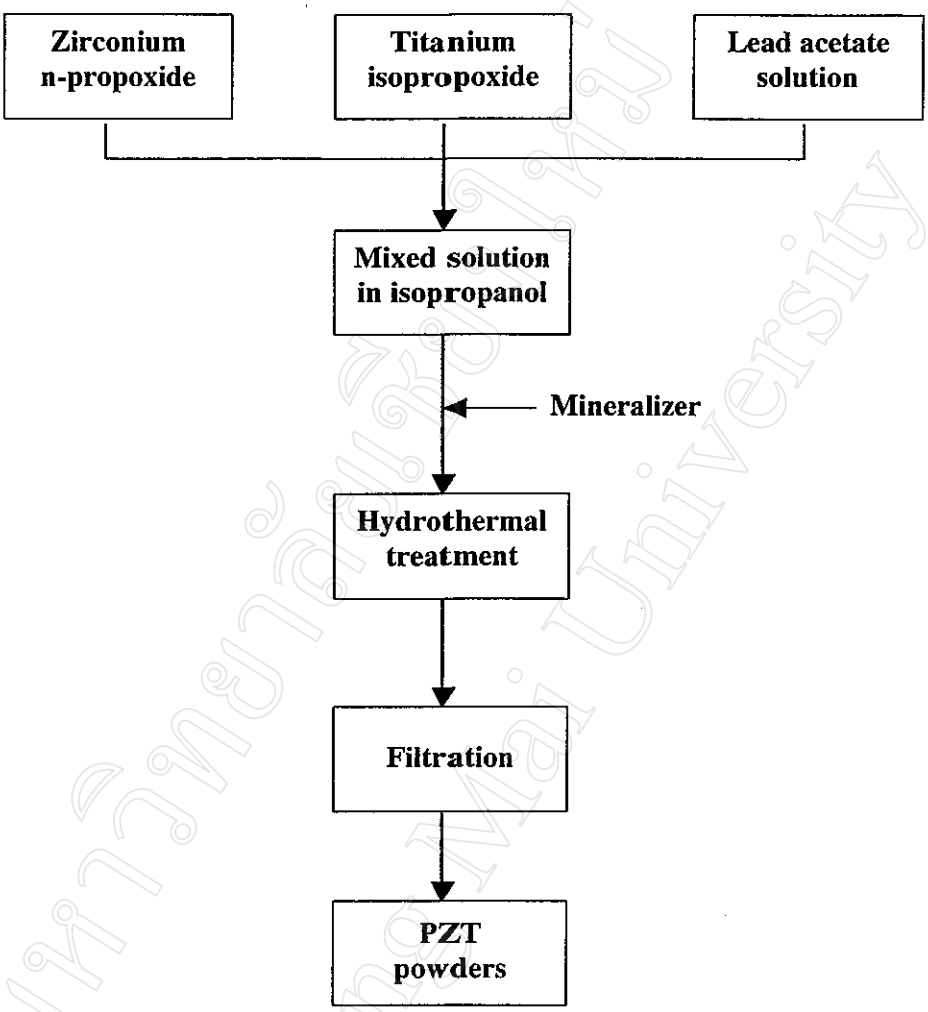

Figure 2.2 Schematic diagram for the preparation of PZT powders by hydrothermal process.

2.3.2 Preparation of PLZT powders

2.3.2.1 Coprecipitation from nitrate solutions

The 0.025 M titanium and 0.025 M zirconium precursor solutions were mixed together. An aqueous mixed solution of 0.025 M lead nitrate and 0.025 M lanthanum nitrate in deionized water was then added to the titanium and zirconium precursor solution in the ratio theoretically required to obtain the desired PLZT composition. The mixed solution was heated to 75 °C. Ammonia solution was then added to adjust pH of the solution to be neutral. Then, the solid portion was separated from the solution by precipitating with ammonia solution. The solid portions were dried at 100 °C for 12 hours and calcined at 550 to 800 °C for 2 hours.

2.3.2.2 Hydrothermal process

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 time varied from 6 to 24 hours.

2.4 POWDERS CHARACTERIZATION

2.4.1 Thermal Analysis (TG-DTA)

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

Differential thermal analysis (DTA) was 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 powders were studied by X-ray diffractometry.

Sample preparation

Crystallographic and phase analyses were performed on an X-ray diffractometer (D 5000, Crystal Structure Limited (CSL)) operating at 25 kV and 20 mA, using CuK_α radiation. The detection range of 2θ values was 20° to 60° with scan step increments of 0.1°. 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 powders were investigated using scanning electron microscopic technique.

Sample preparation

The particle size, morphology and microstructure of PZT powders were characterized by scanning electron microscope (JEOL JSM 840A). The powders sample were dispersed in absolute ethanol using 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, and an accelerating voltage of 5 kV was used.

2.4.4 Transmission Electron Microscopy (TEM)

The particle size and morphology were characterized using transmission electron microscopic technique.

Sample preparation

The particle size and morphology were characterized by transmission electron microscope (JEOL JEM 1200 EXII). TEM characterization was performed using bright field imaging and selected area diffraction. The TEM samples were prepared by dispersing a powder sample in deionized water using ultrasonic agitation, then dropping some of the powder particles on a 100-square-mesh copper grid.

2.4.5 Particle Size Distribution Analysis

The particle size distribution was measured using a particle size analysis.

Sample preparation

The particle size distribution was measured using a particle size analyzer (Malvern Masterizer S219), which detection limit was above 0.1 μm. The samples were prepared by dispersing the PZT powders in deionized water using a high intensity ultrasonic probe. The optical model used for calculating the particle size distribution is based on refractive index of ZrO_2 (2.40 mm) which is the lowest beam length. (refractive index of TiO_2 is 2.50 and PbO is 2.61 mm). Both the differential and cumulative particle size distributions were calculated in term of the number and volume percentage.

2.4.6 Atomic Absorption Spectrophotometry (AAS)

The impurities in PZT powders were determined by atomic absorption spectrophotometry. This method allowed the simultaneous multielement determination of trace amounts of impurities in the samples.

Standard solution preparation

Atomic absorption spectrophotometer (AA 680) was employed to determine the amounts of sodium, magnesium, potassium, calcium and strontium. Standard stock solution of each element was prepared by pipetting 10 ml of standard stock solution (1000 μgmL^{-1}) into a 100 ml graduated flask and made up to the mark with 1% HNO_3. Then 10 ml of this solution was pipetted into another 100 ml graduated flask and made up the mark with 1% HNO_3. Dilute successively five portions of these solutions to give five standard stock solution concentrations (at 1000, 100, 10, 1 and 0.1 μgmL^{-1}). The standard stock solutions were measured by AAS, the calibration curve of each element was plotted by the absorption against concentration of the solution.

Sample solution preparation

Sample solution was prepared by digest 0.5000 g of PZT powders in 10 ml concentrated nitric acid, 50 ml of 2 M nitric acid and 15 ml concentrated hydrochloric acid and heated gently on a hot plate. 15 ml of deionized water was added into the solution until the sample dissolved completely. Then the sample solution was transferred to a 250 graduated flask, made up to the mark with 1% HNO_3, and measured by AAS.

2.4.7 Determination of Lead to Zirconium to Titanium ratio in PZT powders

The amounts of lead (Pb), zirconium (Zr) and titanium (Ti) were determined by gravimetric technique.

Dissolution of PZT powders:

0.5 gram samples of nitrated-PZT powders were digested in the 20 ml nitric acid (diluted with deionized water at 1:1 v/v), heated to 100° C for 1 hour. Then 10 ml sulphuric acid was added and heated to 100 °C. The solution was cooled down, and 100 ml deionized water was added into the solution and the solution was boiled for 5-10 minutes. The solution was cooled down again and the solid was separated from the liquid portion by filtration. The solid part was washed with sulphuric acid which diluted with deionized water at 1:9 v/v. Then this solid part was used to analyze the amount of Pb while the solution was used to analyze the amounts of Ti and Zr in the nitrated-PZT powders. Figure 2.3 shows the schematic diagram of the dissolution of PZT powders.

Analysis of lead:

The solid portion was redissolved in ammonium acetate solution and boiled. This solution was filtered and washed with hot water. 2 ml acetic acid and deionized water was added into the solution until the final volume was 150 ml. This solution was heated to 100 °C. An excess amount of potassium chromate was added to ensure complete precipitation of lead chromate ($PbCrO_4$). After cooling down, the lead chromate was then separated from the solution by sintered glass crucible porosity 4, washed with hot water and ethanol, dried at 110 °C and weighed. Figure 2.4 shows the schematic diagram of the analysis of lead.

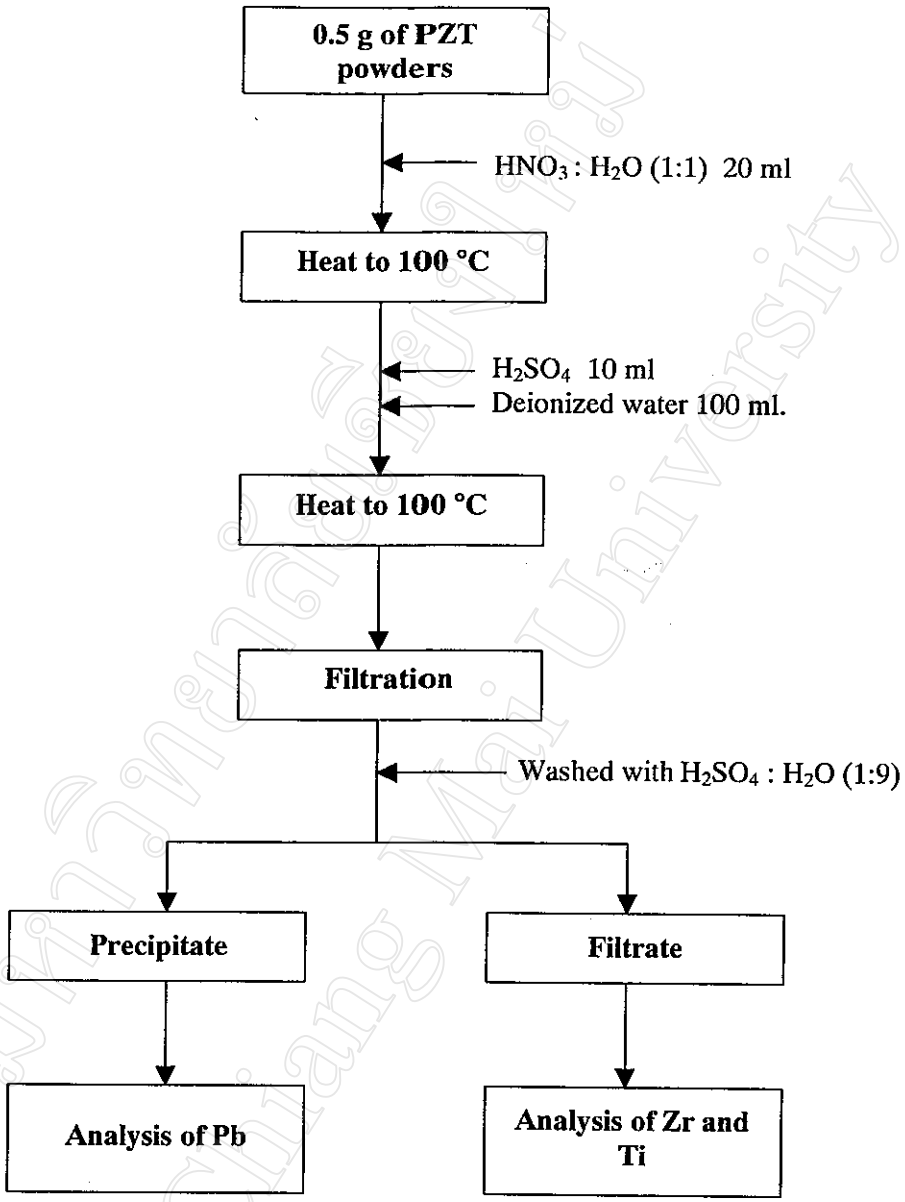

Figure 2.3 The schematic diagram for the dissolution of PZT powders.

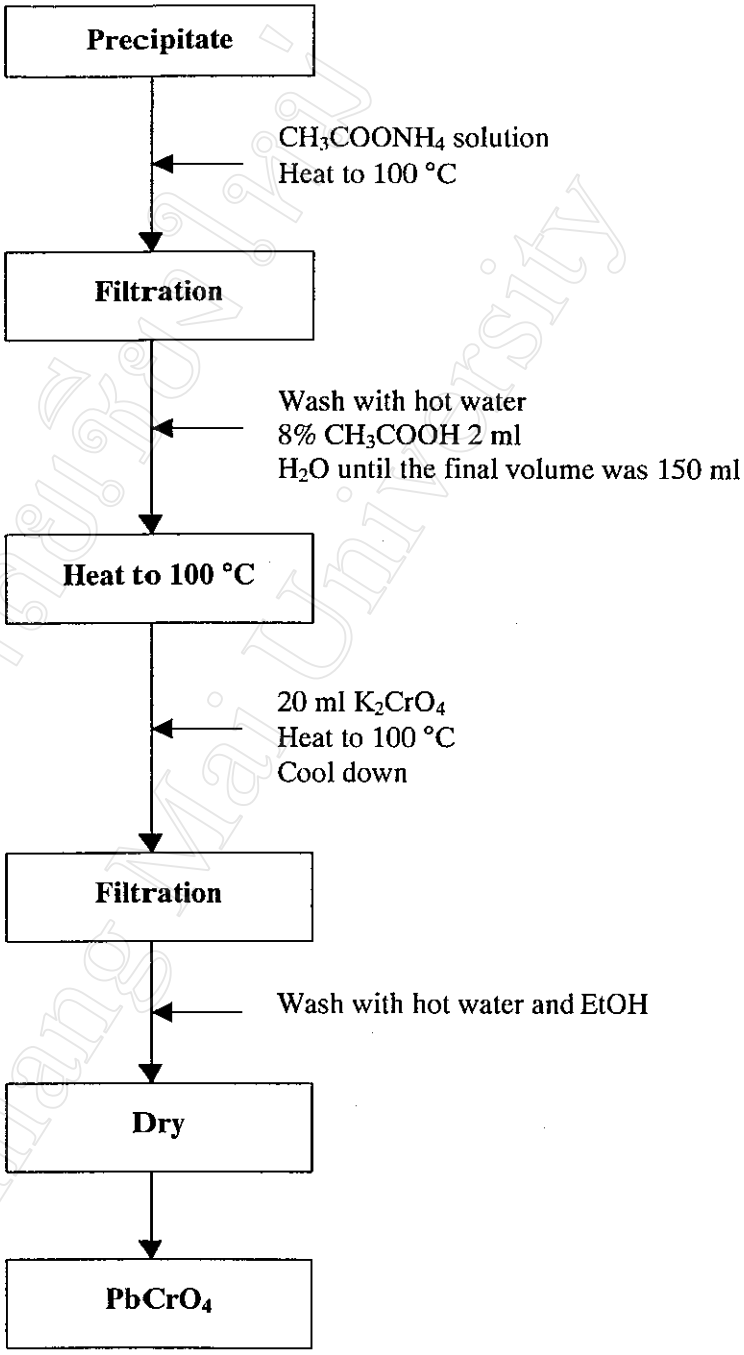

Figure 2.4 The schematic diagram of the analysis of leadas lead chromate.

Analysis of titanium:

Standard titanium solution preparation

Standard curve of titanium solution was prepared by pipetting 1 mg/ml of standard titanium solution at 1, 2, 3, 4 and 5 ml into the 100 ml volumetric flasks. 2 ml sulphuric acid, 1 ml phosphoric acid and 2 ml hydrogen peroxide were added each flask and deionized water was added until the final volume was 100 ml. After 15 minutes, the absorbance of the solution was detected in the range of 400 to 450nm by a UV-visible spectrophotometer.

Sample solution preparation

2 ml sulphuric acid, 1 ml phosphoric acid and 2 ml hydrogen peroxide were added to 5 milliliters of the filtrate in 100 ml volumetric flask. Deionized water was added into the flask to adjust the final volume to be 100 ml. After 15 minutes, the absorbance of the solution was detected and compared to the absorbances of a standard titanium curve.

Analysis of zirconium:

The zirconium content of the remaining solution was determined by precipitation with cupferron reagent. 5 ml sulphuric acid was added into the 50 ml of the filtrate and temperature of the solution was cooled below 10 °C. Then, 30 ml of 6% cupferron was added into the solution. After filtration, the precipitate was burnt. The mass after ignition was the sum of both titanium dioxide and zirconium dioxide. The mass of zirconium was calculated by subtracting the titanium mass values

obtained from the spectrophotometric analysis. Figure 2.5 shows the schematic diagram for the analysis of zirconium.

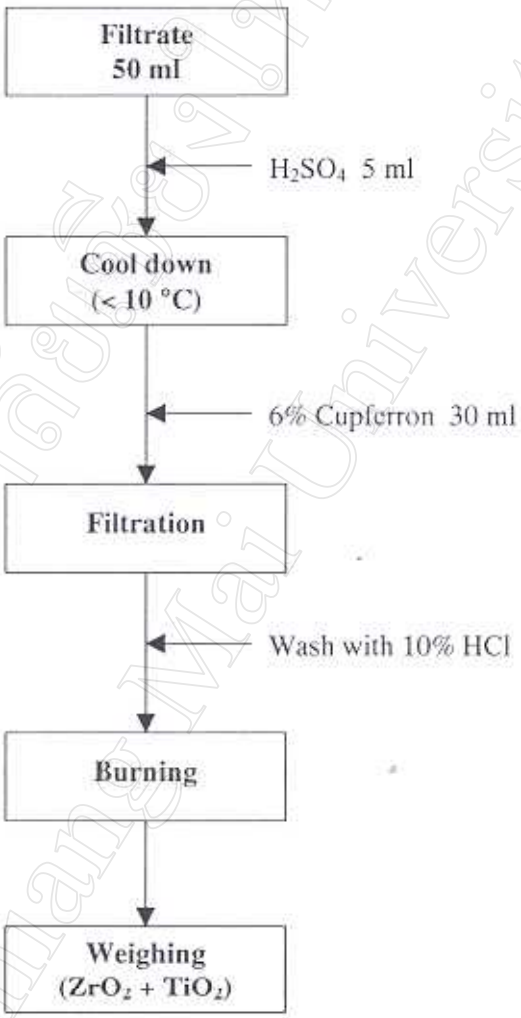

Figure 2.5 The schematic diagram for analysis of zirconium.

2.5 CERAMICS CHARACTERIZATION

2.5.1 Ceramics preparation

PZT powders were pressed in a 2 cm cylindrical die, the pressure appliedwas 3 MPa. The green pellets were placed in an alumina crucible. The specimens were embedded in 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 Hot-pressing process

24 g of PLZT at 9 and 10 mole % lanthanum were sent to Fraunhofer Institute for Ceramics Technology and Sinterwork (Fraunhofer Institut fuer Keramische Technologien and Sinterwerkstoffe), in Dresden, Germany, for hot-pressing process. The powders were put in the graphite mold. The condition for hot pressing was 1250 °C, 4 hours at 30 MPa under argon atmosphere.

2.5.3 X-ray Diffraction (XRD)

The phase present after sintering was identified on an X-ray diffractometer (D 5000, Crystal Structure Limited (CSL)) operating at 25 kV and 20 mA, using CuK_{α} radiation. The detection range of 2θ values was 20° to 60° with scan step increments of 0.1°.

2.5.4 Scanning Electron Microscopy (SEM)

The sintered microstructure of PZT ceramics was studied by scanning electron microscopic technique (JEOL JSM 840A).

2.5.5 Measurement of shrinkage

Shrinkage was measured by compared 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.

2.5.6 Measurement of density

The density of sintered pellets was measured by an immersion technique and calculated using Archimides principle. A dry sample was weighed and then submerged in the hot distilled water for 2 hours, to ensure that all-open porosity within the pellets were filled. The saturated pellets were first weighed at the room temperature in 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.

2.5.7 Measurement of dielectric constant

The dielectric constant of sintered pellets was measured at room temperature using Impedance/Gain-Phase Analyzer (HP 4194A) and Dielectric Test Fixture (HP 16451B) for their capacitance.

The dielectric constant, or relative permittivity (ε_r) were calculated using the following equation:

$$\varepsilon_r = \frac{C \cdot t}{A \cdot \varepsilon_o}$$

Where ε_r is the relative permittivity of piezoelectric material,

ε_0 is the relative permittivity of free space (8.854×10^{-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^3),

C is the measured capacitance at 1 kHz (F)