

Chapter 3

Experimental work

The experimental technique of sample preparation and the measurements for physical, electrical and optical properties as well as microstructure investigation are described in this chapter.

3.1 Preparation of powder and polycrystalline PLZT

All chemicals employed are of reagent grade and were listed in Table 3.1. PLZT (3/52/48) or $\text{Pb}_{0.97}\text{La}_{0.03}\text{Zr}_{0.5161}\text{Ti}_{0.4764}\text{O}_3$ ceramics with 0.5 at.% of various dopants were synthesized by a conventional oxide mixing process. Excess lead oxide (2 mol%) was used to compensate lead loss and to achieve high density ceramics.^(50,51) The flow chart for oxide mixing technique used in this study is shown in Fig. 3.1. In this method, raw materials were mixed in the calculated ratio to achieve the desired composition and ball milled in a polypropylene bottle with zirconia balls, distilled water and 0.1 % of Elotex-50E100 as a dispersant for 10 h. After drying at 110°C, the mixture was calcined to tetragonal perovskite phase forming in a closed alumina crucible at 950°C for 10 h. The calcination curve is shown in Fig. 3.2. The calcined powder was further ball milled with 1 wt% PVA binder (molecular weight 15,000) for 10 h. The powder was then dried at 110°C and screened through a sieve (number 100 mesh). The dried powder was pressed at 80 MPa into pellets (12 mm in diameter and 2.5 mm in thickness) and then sintered in a closed alumina crucible at 1250°C for 2 h. In order to provide PbO atmosphere during sintering, 1 g of PbZrO_3 as a lead source was put in a small alumina boat beside the pressed pellets. The sintering curve is shown in Fig. 3.3.

Table 3.1 Component oxide powders and chemicals used in synthesizing PI.ZT ceramics

Materials	Grade	Manufacturer
Lead oxide PbO	99.0%	Fluka
Lanthanum oxide La ₂ O ₃	99.98%	Fluka
Zirconium dioxide ZrO ₂	~3% HfO ₂	Fluka
Titanium dioxide TiO ₂	99.5%	Unilab
Chromic oxide Cr ₂ O ₃	99.8%	Riedel-De Haen AG
Cupric oxide CuO	>98%	Fluka
Barium carbonate BaCO ₃	99.0%	J.T. Baker
Ferric oxide Fe ₂ O ₃	>98.0%	Fluka
Zinc oxide ZnO	>99.0%	Fluka
Manganese oxide Mn ₂ O ₃	99%	Aldrich
Ammonium metavanadate H ₄ NO ₃ V	>99.0%	Fluka
Lithium carbonate Li ₂ CO ₃	>98.5%	M & B
Potassium carbonate K ₂ CO ₃	>99.0%	Fluka
Nickel(II) sulfate NiSO ₄ .6H ₂ O	>99%	Fluka
Cobalt(II) nitrate Co(NO ₃) ₂ .6H ₂ O	99%	Riedel-De Haen AG
Strontium carbonate SrCO ₃	98+	Aldrich

Table 3.1 (cont.) Component oxide powders and chemicals used in synthesizing PLZT ceramics

Materials	Grade	Manufacturer
Stannic oxide SnO ₂	99.9%	Aldrich
Bismuth oxide Bi ₂ O ₃	99.5%	Riedel-De Haen AG
Boron oxide B ₂ O ₃	>98%	Fluka
Yttrium oxide Y ₂ O ₃	99.99%	Kanto Chemical
Tungsten oxide WO ₃	99+%	Aldrich
Niobium oxide Nb ₂ O ₅	>99.95%	Kanto Chemical
Selenium oxide SeO ₂	99%	J.T. Baker
Gadolinium oxide Gd ₂ O ₃	99.9%	Aldrich

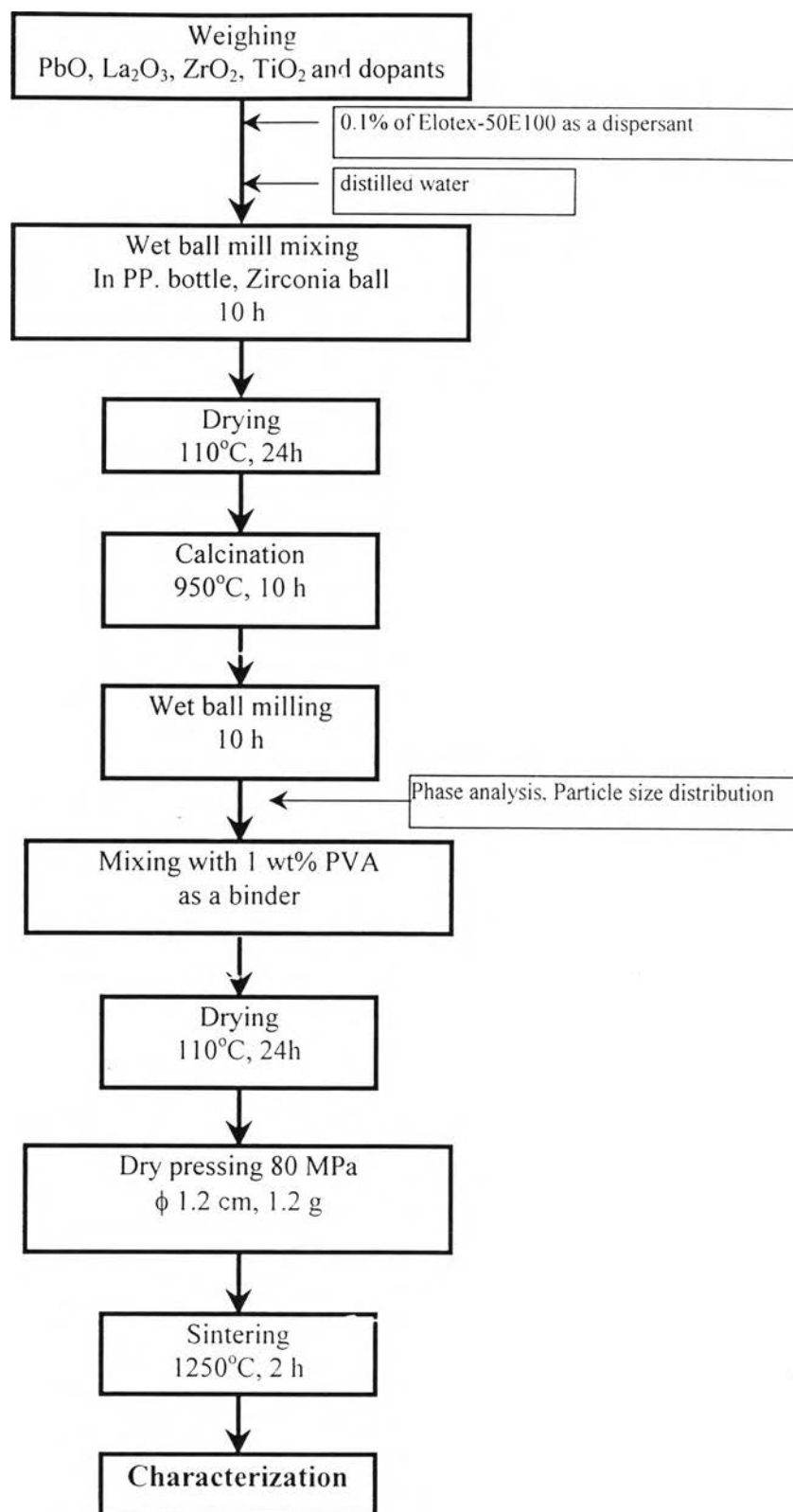


Fig. 3.1 Flow diagram of sample preparation of PLZT ceramics by a conventional oxide mixing process

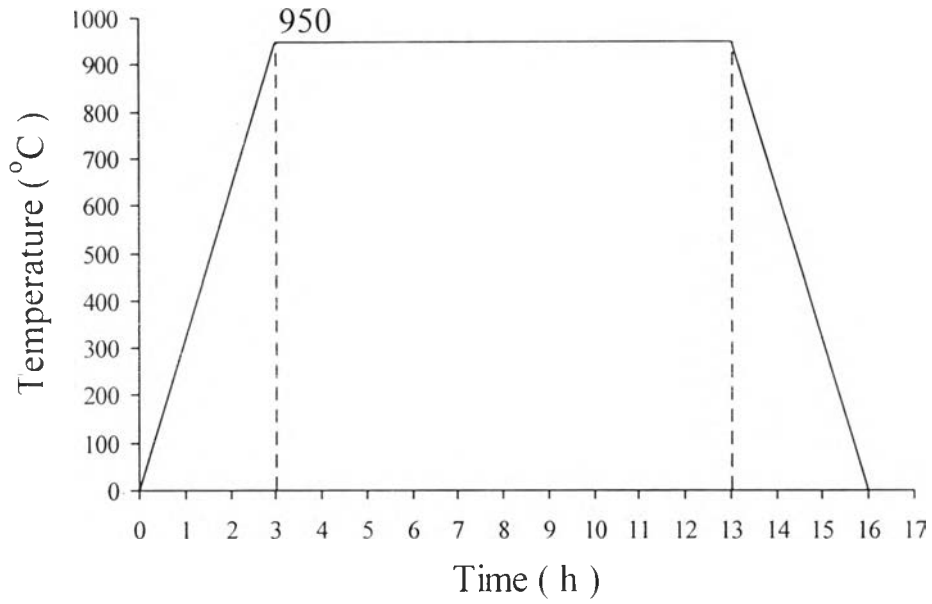


Fig. 3.2 Firing curve for the calcining of PLZT powder

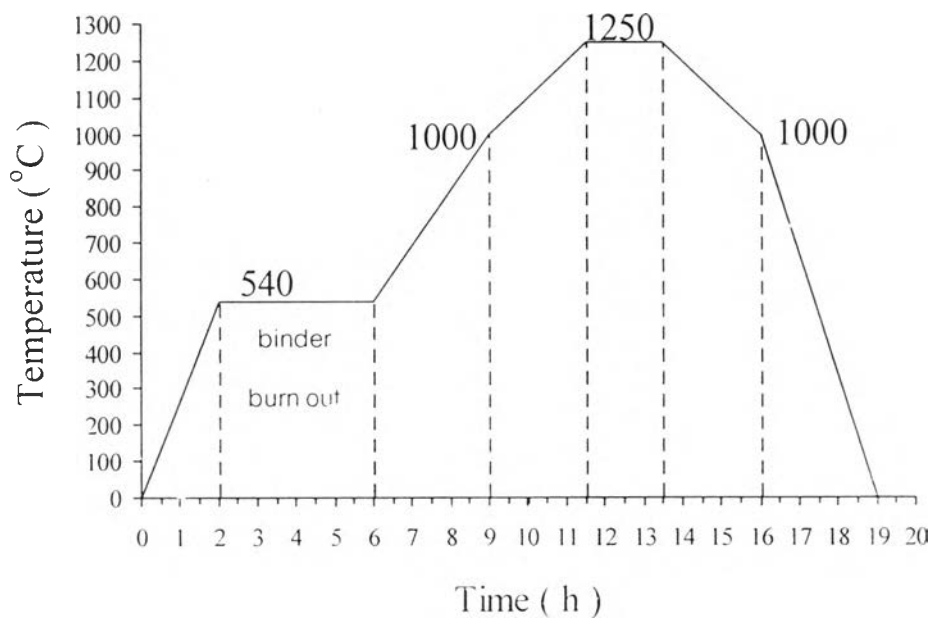


Fig. 3.3 Firing curve for the sintering of pressed-PLZT pellets

3.2 Characterization of PLZT ceramics

3.2.1 Phase identification by X-ray diffraction

Phase determination of calcined powders (after milling for 10 h) and sintered ceramic samples were studied using X-ray diffraction. The conditions for measurement were $\text{CuK}\alpha$ radiation ($\lambda=1.5418\text{\AA}$) with a tube voltage and current of 30 kV and 30 mA, respectively. Prior to the measurement, the X-ray diffractometer (JEOL: JEOL-3530) was calibrated using high purity silicon as an external reference standard. The sample was scanned for 2θ range of $20\text{-}80^\circ$ at 0.04 degree for step angle and 0.50 second for count time.

XRD patterns of calcined powder were investigated to determine the single phase perovskite PLZT with fully crystallization. In addition, XRD patterns of sintered PLZT pellets with polished surface were investigated for the other phases which may take place after firing at higher temperature.

3.2.2 Density determination

3.2.2.1 Bulk density

Bulk density of sintered PLZT pellets was determined by Archimedes method. Samples were boiled in distilled water for 2 h and cooled to room temperature which then were cured for another 12 h. The dry weight W_d , saturated weight W_{sat} and suspended weight W_{sus} were taken and used to calculate bulk density following the ASTM standard (Designation C 20-00).

$$\text{Bulk density} = \frac{W_d}{W_{\text{sat}} - W_{\text{sus}}} \rho \quad (3.1)$$

where ρ is water density at the measurement temperature (0.99568 g/cm^3 at 30°C).

3.2.2.2 Theoretical density

Theoretical density of sintered PLZT pellets were calculated using the following equation

$$\text{Theoretical density} = \frac{M}{V \cdot N_A} \quad (3.2)$$

where M is the molecular weight (g/mol),

V is the lattice volume (cm³/molecule) calculated from the (002) and (200) peaks of the XRD patterns,

and N_A is the Avogadro's number (6.02254x10²³ molecule/mol)

3.2.3 Microstructure examination by Scanning Electron Microscope (SEM)

Morphology of calcined powder and microstructure of sintered PLZT ceramics were examined with a Scanning Electron Microscope (JEOL: JSM-5410). Surface of the sintered ceramics were polished with increasing fineness of SiC paper and finished with 1 μm diamond paste. Thermal etching of polished surface was then performed by heating the samples to 1150°C and keeping for 10 min in a closed alumina crucible under PbO atmosphere. The etching temperature was chosen to be lower than the sintering temperature in order to prevent the significant grain growth. Surfaces of all the samples were gold-coated by sputtering for 120 sec to reduce the charging during SEM observation. The average grain sizes were determined by a line intercept method following the ASTM standard (Designation E 112-96).

3.2.4 Electronic properties

3.2.4.1 Dielectric constant measurement

Samples for the dielectric measurement were polished with increasingly fine grades of SiC paper to about 10 mm in diameter and 1 mm in thickness. Silver paint solution (air dried) was applied on both sides of the pellet as an electrode. The dielectric constant (K) and dissipation factor ($\tan \delta$ or D) of the prepared samples were measured at room temperature using an impedance analyzer (Hewlett Packard: 4192A LF Impedance Analyzer) at five different frequencies of 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz. The dielectric constant was calculated from the measured capacitance value from the following equation

$$K = \frac{C t}{\epsilon_0 A} \quad (3.3)$$

where C is the capacitance (Farad),

t is thickness of the sample before applying the electrode,

ϵ_0 is the permittivity of free space (8.854×10^{-12} F/m),

and A is the electrode area (m^2).

3.2.4.2 Piezoelectric constant measurement

Samples for piezoelectric constant (d_{33}) measurement were of the same configuration with the samples for the dielectric constant measurement but they were poled in silicone oil at 120 °C under 2 kV/mm electric field for 10 min. The piezoelectric constant of all the samples were measured with d_{33} meter (Berlincourt Piezo d-meter Model CADT) at an applied vibration frequency of 120 Hz.

3.2.5 Photovoltaic measurement

Samples for photovoltaic measurements were cut to a size of $4 \times 7 \times 1 \text{ mm}^3$ and polished to 1 μm of diamond paste on both $7 \times 4 \text{ mm}^2$ surfaces. Silver paint solution (air dried) electrode were painted on two opposite $7 \times 1 \text{ mm}^2$ surfaces. The specimens were poled with the same conditions as in the piezoelectric constant d_{33} measurement by applying 2 kV/mm electric field in silicone oil at 120 °C for 10 min.

A high pressure, short arc mercury lamp (Ushio Optical Modulex H500) was used as a light source for the photovoltaic measurement. The original lamp radiation was passed through an infrared (IR) blocking filter (Oriel No. 59060) to obtain a light beam with the maximum intensity around 366 nm wavelength. Radiation with this wavelength has been reported to yield the maximum photovoltaic properties^(23,24) This wavelength is near the absorption edge or energy band gap of PLZT ceramics^(28,43).

Fig. 3.4 shows the experimental setup for photovoltaic measurement. Photovoltage and photocurrent were determined from the plotted curve between the measured current with an applied voltage (-100 and $+100 \text{ V}$) while the samples were illuminated. Photovoltage was determined in an open circuit state from the intercept of the applied voltage axis while photocurrent was obtained in a short circuit state from the intercept of the current axis. Fig. 3.5 illustrates the determination of photocurrent and photovoltage from the plot.

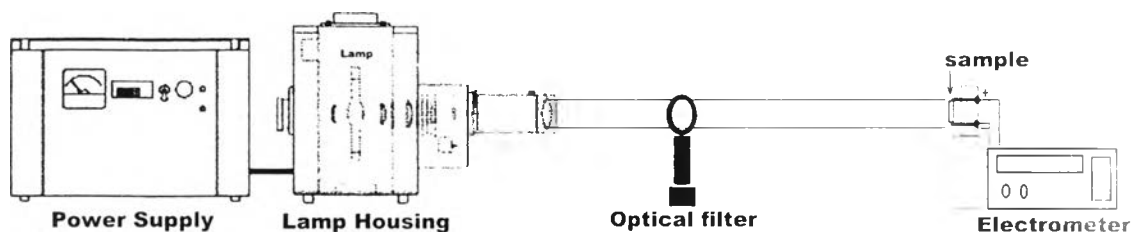


Fig. 3.4 Experimental set-up for photovoltaic measurement

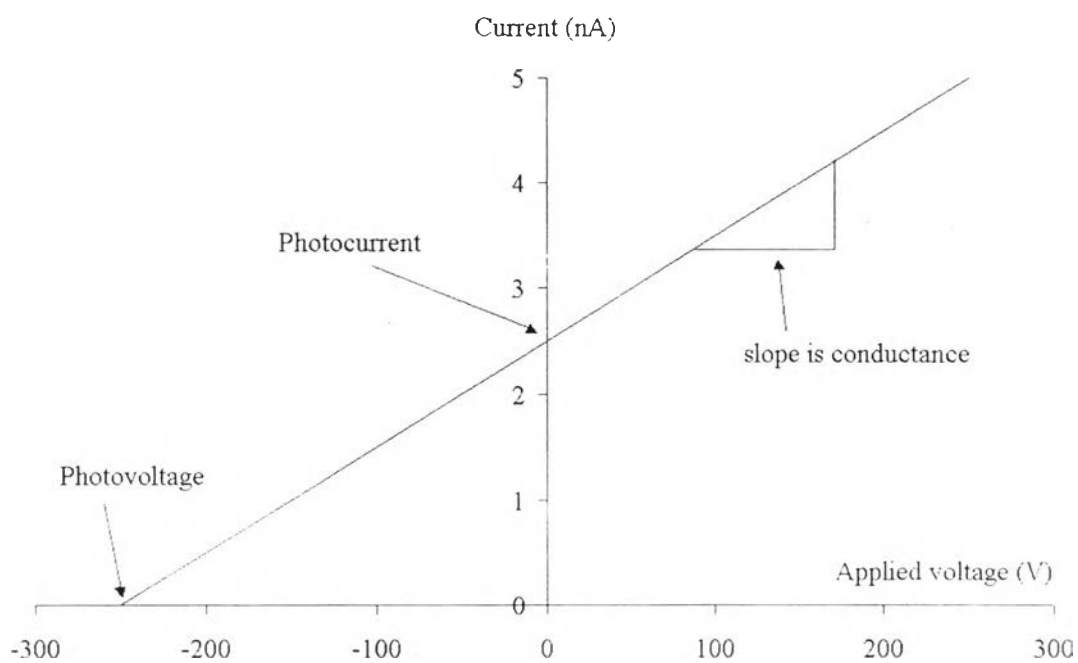


Fig. 3.5 Schematic diagram showing the relationship between the measured photocurrent and applied voltage

3.2.6 Optical absorption edge by UV/VIS Spectrophotometer

Optical transmission spectra of PLZT ceramics were measured at room temperature with an excitation wavelength of 200-900 nm using the spectrophotometer (Jenway 6405 UV/Vis Spectrophotometer). The disk-shaped samples were mounted in acrylic resin and polished to a thickness of 0.05 mm. The mounted samples were immersed in liquid paraffin to reduce light scattering at the surface⁽⁴⁷⁾.

Wavelength of the transmission spectra was converted to photon energy by

$$E = h \nu \quad (3.4)$$

or

$$eV = 1239.8 / \lambda \quad (3.5)$$

where E is photon energy (electron volt: eV),
 h is the Plank's constant (6.626×10^{-34} J.s),
 ν is light frequency (Hz),
 and λ is wavelength (nm).

The optical absorption edge or band gap energy is the energy near the last wavelength, which has enough energy to excite electron in the valence band to the conduction band of the materials as shown in Fig. 2.8. The band gap energy is given by Eq. 2.9 in chapter 2.