

CHAPTER III EXPERIMENTAL



3.1 Materials

Titanium dioxide and nitric acid were purchased from Carlo Erba (Val de Reuil, France) and used as received. Ethylene glycol (EG) was purchased from Malinckrodt Baker, Inc. (USA) and purified by fractional distillation at 200°C under nitrogen atmosphere, before use. Triethylenetriamine (TETA) was purchased from Facai Polytech. Co. Ltd. (Bangkok, Thailand) and distilled under vacuum (0.1 mm/Hg) at 130°C prior to use. Acetonitrile was purchased from Lab-Scan Company Co. Ltd. and purified by distilling over calcium hydride powder. Sodium hydroxide was purchased from Asia Pacific Specialty Chemical Limited. Zirconium (IV) hydroxide and lead acetate trihydrate (99%) were purchased from Aldrich Chemical Company, Inc. (USA) and Fluka chemical (Buchs, Switzerland), respectively. Both were used as received.

3.2 Experimental Instruments

Thermogram (TGA, Dupont) was obtained to identify the thermal properties and the percent ceramic yield. Fourier Transform Infrared spectra (FTIR, Bruker) were obtained to the functional groups. X-ray Diffraction (XRD) patterns (D/MAX-2200H Rigaku diffraction) was obtained to identify crystallinity, the percent perovskite content and the structure of PZT. Surface area measurement (Autosorp-1 Quantachrome Corporation) via the Brunauer-Emmett-Teller (BET) method were obtained to identify surface area. Scanning Electron Microscope (JEOL 5200-2AE (MP 15152001) was used to determine the product morphology. Electron probe microanalysis (EPMA, Oxford SEM/EDS) was used to determine the morphotropic phase boundary (MPB) of the Zr/Ti ratio.

3.3 Precursor Preparation

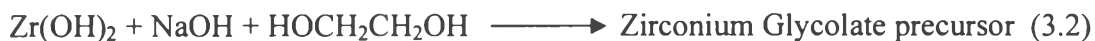
3.3.1 Titanium Glycolate or Glycotitanate (Phonthammachai *et al.*, 2003)

Titanium Glycolate was prepared by reacting titanium dioxide (TiO_2) with ethylene glycol using triethylenetetramine (TETA) as catalyst. The mixture was allowed to react at 200°C for 24 h, followed by filtering the unreacted TiO_2 . The obtained mixture solution was then distilled to remove excess ethylene glycol and TETA under vacuum (10^{-2} torr) at 110°C for 12 h. to give crude powder product. The powder was then washed with acetonitrile until the filtrate had no color to yield white powder which was kept in a dessicator under vacuum at room temperature for further use.



3.3.2 Zirconium Glycolate or Sodium Tris (glycozirconate) (Ksapabutr *et al.*, 2004)

The reaction of zirconium hydroxide ($\text{Zr}(\text{OH})_2$) and ethylene glycol, using sodium hydroxide (NaOH) as catalyst was carried out at 200°C for 12 h. Precipitate obtained was washed off with acetonitrile and methanol to eliminate excess ethylene glycol and to obtain white powder product which was kept in a vacuum dessicator for further use.



3.3.3 Lead Glycolate

The mixture of lead (II) acetate trihydrate, ethylene glycol and TETA, as catalyst, was heated at 200°C to distill off excess ethylene glycol. The reaction was complete within 2 h followed by distilling TETA at 120°C under vacuum (10^{-2} torr) for 30 min. The crude product was precipitated and washed with acetonitrile to obtain gray powder product which was kept in a vacuum dessicator for further use.



All synthesized precursors were characterized using TGA / DTG and FTIR.

3.4 Lead zirconate titanate (PZT, $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$) Preparation

3.4.1 Preparation of PZT via the Sol-Gel Process

Lead zirconate titanate was prepared by adding a solvent into three precursors and by varying the following factors:

- Type of solvent to be added into the precursors.
- pH (2-4)
- Temperature (40- 90°C)
- Time period during gellation (1-10 h)

Lead Glycolate, Titanium Glycolate and Zirconium Glycolate were used and calculated to prepare PZT at the composition near the morphotropic phase boundary (MPB, $\text{Zr}/\text{Ti} = 52/48$). The mixture of all three precursors was added at 0.5 M-5 M of nitric acid solutions and 0.5 M-2.5 M of sodium hydroxide solutions, at various temperature (40-90°C) for sol-to-gel conversion, and at various temperature (600-1300°C) and time (0.5-3 h) for the gel calcination. To obtain transparent gel three precursors were dissolved in nitric acid and sodium hydroxide solutions.

3.4.1.1 Various concentrations of nitric acid and sodium hydroxide solutions, the pH of solution and the volume ratio of nitric acid and sodium hydroxide.

All three precursors were added to a HNO_3 solution followed by NaOH solution to obtain the final pH between 2-4. The conditions studied are summarized in Table 3.1.

Table 3.1 Variation of nitric acid and sodium hydroxide solution ratio

Sample #	HNO ₃		NaOH	
	Amount (μ l)	Concentration (M)	Amount (μ l)	Concentration (M)
1	5000	0.5	3500-2800	0.5
2	3500	1.0	2900-2000	1.0
3	3000	1.5	2500-1500	1.5
4	2700	2.0	2000-1000	2.0
5	2500	2.5	1500-800	2.5
6	1500	5.0	1000-500	5.0

3.4.1.2 Various temperatures for sol-to-gel conversion.

All above sols prepared in 3.4.1.1 were heated in a water bath at various temperatures of 40°, 50°, 70° and 90°C to form gels.

3.4.1.3 Various calcination temperatures and times.

White powder occurred after preheated the PZT gel at 110°C for 3 h in the oven followed by calcination at various temperatures of 400°-1000°C with 100°C interval. Each temperature was set for calcinations times of 2, 1.5 and 1 h. After the calcinations, the white powder changed to slight yellow powder.

All products were characterized using XRD, FTIR and SEM-EDS. The thermal properties of PZT dry gel were investigated using TGA-DTG. The macromolecule size of PZT before and after calcination was characterized using SEM.

3.4.2 Preparation of PZT via the Sol-Gel Process with Microwave Technique

The study of nitric acid and sodium hydroxide ratio (section 3.4.1.1) showed that 5000 μ l of 2.5 M HNO₃ and 2000 μ l of 2.5 M NaOH was the optimal

condition for obtaining a transparent gel. All glycolate precursors were dissolved in this ratio. Homogenous solution resulted after aging the solution for a duration of 5 min.

3.4.2.1 Various reaction temperatures and times in microwave.

Various microwave temperatures and times from 130°-180°C and from 5-25 h, respectively, were studied. After heating the solution with microwave, white precipitate occurred. The white precipitate was separated, dried overnight and preheated at 110°C for 3 h.

3.4.2.2 Various calcination temperatures and times.

The dry white powder from microwave was calcined at 700°, 800° and 900°C for 1, 1.5 and 2 h at the heating rate of 5°C/min. The powder before and after calcination was characterized by XRD to determine PZT perovskite structure, FTIR to observe the residue organic groups, SEM to study the macromolecular size, and TGA-DTG to study the thermal properties.