

CHAPTER III

EXPERIMENTAL

3.1 Materials

UHP grade nitrogen, 99.99% purity, was obtained from Thai Industrial Gases Public Company Limited (TIG). Lead acetate trihydrate $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ containing 99.5% purity was purchased from Asia Pacific Specialty Chemical Limited (Australia) and used as received. Titanium dioxide was purchased from Sigma-Aldrich Chemical Co., Ltd. (USA). Zirconium (IV) hydroxide $\text{Zr}(\text{OH})_4$ containing 88.8% ZrO_2 was purchased from Aldrich Chemical Co., Inc. (USA). Ethylene glycol (EG) was purchased from Farmitalia Carlo Erba (Barcelona) or Malinckrodt Baker, Inc. (USA), and purified by fractional distillation under nitrogen at atmospheric pressure, 200°C before use. Triethylenetetramine (TETA) as purchased from Facai Polytech. Co., Ltd. (Thailand) and distilled under vacuum (0.1 mm/Hg) at 130°C prior to use. Acetonitrile was purchased from Lab-Scan Co., Ltd., and distilled over calcium hydride powder by standard technique.

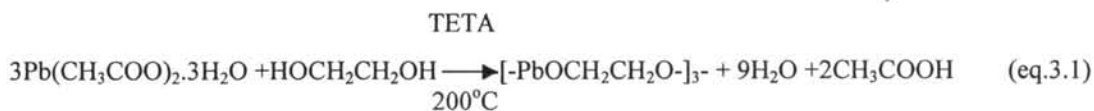
The starting raw materials, lead glycolate, titanium glycolate and sodium tris(glycozirconate) were synthesized by the oxide one pot synthesis process (OOPS) which was less moisture sensitive.

3.1.1 Precursor Synthesis

3.1.1.1 *Lead Glycolate*

Lead glycolate was synthesized via the OOPS process. A mixture of lead acetate trihydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, 0.1 mol, 37.9 g), ethylene glycol (EG, 0.1 mol, added excess 50 cm^3) and triethylenetetramine (TETA, 0.1 mol, 14.6 g) acted as a catalyst when heated at the boiling point of EG under N_2 in a thermostated oil bath. The excess EG was slowly distilled off as to remove water liberated from reaction. After heating at 200°C for 1 h, the solution color changed to be yellow or golden brown. The reaction mixture was cooled to obtain a crude precipitate product followed by filtration with acetonitrile. The light bronze solid product was obtained and dried in a vacuum desiccator (0.1 mm Hg) at room

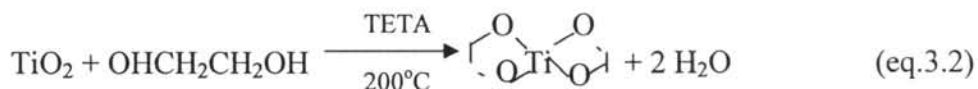
temperature and characterized using FTIR, ^{13}C -NMR, FAB⁺-MS, TGA, pycnometer and Impedance Analyzer.



FTIR bands observed were: 2778-2829 cm^{-1} corresponding to the C-H stretching of ethylene glycol bidentate ligand, 1086 and 1042 cm^{-1} $\nu(\text{C-O})$ stretching, 682 and 879 cm^{-1} (C-O-Pb) stretching and 573 cm^{-1} (s, Pb-O) stretching. Due to the insolubility of lead glycolate powder in all organic solvent ^{13}C -NMR solid state mode showed only one single peak at 68.639 ppm, corresponding to ethylene glycol ligand (-PbOCH₂CH₂O-). TGA showed one sharp mass loss transition at 300°C and gave a 82.50% ceramic yield which is close to the theoretical yield of 83.50%. FAB⁺-MS showed the highest m/e at 801 of $[-\text{PbOCH}_2\text{CH}_2\text{O}-]_3^-$ and 505 of $-\text{CH}_2\text{OPbOCH}_2\text{CH}_2\text{OPb}- + \text{H}^+$. XRD showed phase transformation of lead glycolate from room temperature to 800°C of α -PbO and β -PbO as those recorded in the Joint Committee on Powder Diffraction Standards (JCPDS). The dielectric constant, electrical resistivity and conductivity are 7.42-22.96, 10^{11} ohm.m and $4.28-7.99 \times 10^{-12}$ ohm⁻¹m⁻¹ at 10^6 Hz., respectively.

3.1.1.2 Titanium Glycolate

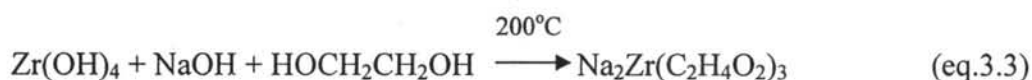
Titanium glycolate was also synthesized via the OOPS process. A mixture of titanium dioxide (TiO₂, 0.025 mol, 2 g) and TETA (0.0074 mol, 3.95 g) mixed with ethylene glycol (EG added excess 25 cm³) was stirred vigorously and heated at the boiling point of EG for 24 h, followed by separating the unreacted TiO₂ from the solution part. The excess of EG and TETA were removed by the vacuum distillation to obtain a crude precipitate. The white solid product was washed with acetonitrile and dried in a vacuum dessicator before characterization using FTIR, TGA.



FTIR bands observed were: 3000-3700 cm^{-1} (with trace of water absorbed in the product), 2860-2986 cm^{-1} (s,vC-H), 1073 cm^{-1} (m, vC-O), 1021 cm^{-1} (s,vC-O). TGA result showed one sharp mass loss corresponding to the decomposition of organic ligand and remaining organic residue around 310°C-350°C and gave 46.8% ceramic yield which is close to theoretical yield of 47.5%.

3.1.1.3 Sodium tris (glycozirconate)

A mixture of 10 mmol (1.59 g) zirconium hydroxide $\text{Zr}(\text{OH})_4$ and 20 mmol (0.08 g) sodium hydroxide (NaOH) were suspended in 35 ml of ethylene glycol (EG). The reaction mixture was heated under nitrogen in a thermostatted oil bath. When the thermostatted oil bath reached to the boiling point of ethylene glycol, the reaction was considered to have commenced. Ethylene glycol was slowly distilled off so as to remove any liberated water from the reaction. After 12 h the solution was virtually clear, indicating reaction was completion. The reaction mixture was cooled, and 2-5% of dried methanol in acetonitrile was added. The product precipitated out as a white solid. The solid was filtered off, washed with acetonitrile and dried under vacuum (0.1 mmHg) at room temperature. The results were observed by FTIR, TGA, FAB^+ -MS, ^{13}C -NMR.



FTIR bands were observed were: 3000-3700 cm^{-1} v(O-H) w, trace of water absorbed in the product, 1600 cm^{-1} the (O-H) bending vibration of the water of hydration, 2873 and 2939 cm^{-1} the v(C-H), 1200-1400 cm^{-1} of methylene groups, 1090 cm^{-1} the (Zr-O-C) stretching vibration mode, 880 cm^{-1} the (C-C) bond deformation, 613 cm^{-1} the (Zr-O) stretching. TGA showed one major thermal decomposition ranging from 350°C to 545°C. The percentage ceramic yield of the

product was 58.41% which is close to the theoretical ceramic yield 58.33%. EA results are 22.41% (Carbon) and 4.23% (Hydrogen) which are close to the theoretical C and H content 22.70 and 3.78 respectively. ^{13}C -NMR found a single peak at 62.6 ppm belonging to the symmetrical carbon chelated glycolate ligand ($\text{CH}_2\text{-O-Zr}$).

3.2 Instrumental

3.2.1 FAB⁺-MS Spectroscopy (MS)

Mass spectra were obtained on a VG Autospec-ultima 707E from Fisons, using a direct probe of the positive fast atom bombardment (FAB^+) mode. Cesium iodide (CsI) was used as a standard for peak calibration. The cesium gun beam, used as an initiator, was set at 2 μA for the optimum resolution. The range studied was set from m/e 20 to 1000.

3.2.2 Elemental Analysis (EA)

The percent elements were obtained from a Perkin Elmer PE 2400 Series II CHNS/O analyzer with combustion and reduction temperatures at 975°C and 500°C respectively and vial receptacle for 1000 runs. The sample was analyzed under air (flowing rate 60 psi) with oxygen as a combustion gas (flowing rate 15 psi) and helium as carrier gas (flowing rate 20 psi).

3.2.3 Thermogravimetric Analysis (TGA)

TGA thermograms were carried out on a Du Pont instrument, Du Pont TGA 2950. Approximately 5-10 mg of sample was placed into a ceramic crucible and heated under atmosphere at a flow rate 10°C/min. The temperature program was stated from room temperature to 1200°C, with a heating rate of 10°C/min.

3.2.4 Nuclear Magnetic Resonance Spectroscopy (NMR)

Solid state ^{13}C -NMR spectra were performed on a Bruker 300 MHz. spectrometer with cross polarization (CP) and magic angle spin (MAS) compatibility in order to study the structure of lead glycolate, titanium glycolate, sodium tris

(glycozirconate), dried lead titanate gel, dried lead zirconate gel, and dried lead zirconate titanate gel. The sample was washed with acetonitrile for several times and vacuum dried for 1 day prior to use.

3.2.5 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared absorption spectra (IR) were recorded on a Bruker FT/IR (model EQUINOX 55) spectrometer using KBr pellets: 1-2 mg of the sample was crushed and mixed with 300 mg of KBr.

3.2.6 X-Ray Diffraction (XRD)

A Phillip electronic analyzer (N.V.1999) consisted of $\text{CuK}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). The system equipped with 2000 wide angle goniometer and a Cu tube for generating a $\text{CuK}\alpha$ 1 radiation ($\lambda = 1.54 \text{ \AA}$) was used to obtain the X-ray diffraction patterns at a generator voltage of 30 kV and a generator current of 40 mA. Nickel filter was used as the $\text{K}\beta$ filter. The goniometer parameters were divergence slit = $1^\circ(2\theta)$; scattering slit = $1^\circ(2\theta)$; and receiving slit = 0.3 nm. A sample (0.1-0.2 g) was spread on a glass slide. A scan speed of $5^\circ(2\theta)/\text{min}$ with a scan step of $0.02^\circ(2\theta)$ were employed during a continuous run in the 10 to $90^\circ(2\theta)$ range.

3.2.7 Scanning Electron Microscopy (SEM)

The scanning electron micrographs were carried out to identify the microstructure of a sample. The samples were characterized using a Jeol scanning electron microscope, model JSM 5200.

3.2.8 X-Ray Microscan

The percentages of chemical compositions of calcined samples were obtained by an X-ray analytical microscope (XGT 2000w, Horiba, Japan).

3.2.9 Impedance Analyzer

The impedance analyzer was used to measure the electrical properties of samples. The samples were investigated by using a Hewlette Packard (Hp) precision LCR meter, model 4284A at 20 Hz.-1MHz.

3.2.10 Raman Spectroscopy

The Raman spectra of powder samples were obtained using a spectrometer (Labram HR 800, DU-420-OE-322).

3.3 Methodology

3.3.1 Lead Titanate Preparation via Sol-Gel : PbTiO₃

The structure of lead titanate PbTiO₃ was composed of mol ratio Pb:Ti:O equal to 1:1:3. A mixture of lead glycolate mixed with titanium glycolate alkoxide precursor was prepared with 1 mol of Pb(II) : 1 mol of Ti(IV). The mixture was mixed into 0.1 M nitric solution (HNO₃) to obtain complex alkoxide sol which was white turbid solution. The transition from sol to gel occurred by adding 1.0 M sodium hydroxide solution (NaOH) to adjust pH to a value 3-4 at room temperature within a few minute. The molar ratios of Pb:Ti between lead glycolate and sodium tris (glycozirconate) precursors at 1:1; 1:2; 1:3; 1:4; 2:1; 3:1 ;4:1 were selected to study the complete sol-gel formation. The gels derived from the complex alkoxide of lead-titanium glycolate were allowed to settle at room temperature and were dried at 50°C within 1-2 days. The color of dried gel was light yellow. After that, the dried gels were calcined at 300°C, 400°C, 600°C, 800°C and 1000°C for 1, 3 and 5 h. Sol-gel products were characterized by FTIR, ¹³C-NMR, SEM, XRD, Raman, TGA, and impedance analyzer.

3.3.2 Lead Zirconate Preparation via Sol-Gel : PbZrO₃

The structure of lead zirconate PbZrO₃ was composed of mol ratio Pb:Zr:O equal to 1:1:3. Sol of complex alkoxide mixture was prepared by mixing lead glycolate in a 0.1 M nitric solution (HNO₃) with sodium tris (glycozirconate) dissolved in water. The white turbid sol formation was obtained when they were poured to react together. The sol to gel transition occurred within a few second when

adding a little amount of water to adjust pH in the range of 8-9 at room temperature. The molar ratios of Pb:Zr between lead glycolate and sodium tris (glycozirconate) precursors at 1:1; 1:2; 1:3; 1:4; 2:1; 3:1 ;4:1 were selected to study the completely sol-gel formation. The gels were allowed to settled at room temperature and dried at 50°C for 2 days to finally obtain a light yellowed gel. The gels were calcined at 200°C, 300°C, 400°C, 500°C, 600°C and 700°C for 1, 2 and 3 h. The dried gels were charaterized by FTIR, ¹³C-NMR, SEM, XRD, Raman, TGA, and impedance analyzer.

3.3.3 Lead Zirconate Titanate Preparation via Sol-Gel : Pb(Zr_xTi_{1-x})O₃

The structure of lead zirconate titanate Pb(Zr_xTi_{1-x})O₃ was composed of the mol ratio Pb:Zr,Ti:O equal to 1:1:3. Sols of complex alkoxide mixture were prepared by mixing lead glycolate and titanium glycolate in a 0.1 M nitric acid solution (HNO₃) with sodium tris (glycozirconate) dissolved in water. The white turbid sol formation occurred when they reacted with each other. The sol to gel transition occurred within a few minute when adding a little amount of water to adjust pH in the range of 5-6 at room temperature. The molar ratios of Pb:Zr:Ti among lead glycolate, sodium tris (glycozirconate), titanium glycolate precursors at 1:0.8:0.2; 1:0.7:0.3; 1:0.6:0.4; 1:0.5:0.5; 1:0.4:0.6; 1:0.3:0.7; 1:0.2:0.8 were selected to study the complete sol-gel formation. The gels were allowed to settle at room temperature and dried at 50°C for 2 days to finally obtain a browned gel. The gels were calcined at 200°C, 300°C, 400°C, 500°C, 600°C, 700°C and 800°C for 1, 2 and 3 h. The dried gels were characterized by FTIR, ¹³C-NMR, SEM, XRD, Raman, TGA, an impedance analyzer.