

CHAPTER VII
A NOVEL ROUTE TO PEROVSKITE LEAD ZIRCONATE TITANATE (PZT)
FROM LEAD GLYCOLATE, SODIUM TRIS (GLYCOZIRCONATE), AND
TITANIUM GLYCOLATE VIA SOL-GEL PROCESS

7.1 Abstract

A perovskite lead zirconate titanate was synthesized by the sol-gel process, using lead glycolate, sodium tris (glycozirconate), and titanium glycolate as the starting precursors. For the mole ratio Pb:Zr:Ti of 1:0.5:0.5 ($\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$), TGA-DSC thermal analysis indicated that the percentage of ceramic yield was 55.8, close to the calculated chemical composition value of 49.5. The exothermic peak occurred at 268°C below the theoretical Curie temperature of 400°C. The pyrolysis of $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ of the perovskite phase was investigated in terms of calcination temperature and time. The structure obtained was of the tetragonal form when calcined at temperatures below 400°C; it transformed to the tetragonal and the cubic forms of the perovskite phase at calcination temperatures above the Curie temperature as verified by X-ray data. The lead zirconate titanate synthesized and calcined at 400°C for 1 h has the highest dielectric constant, the highest electrical conductivity, and the dielectric loss tangent of 10190, $0.803 \times 10^{-3} (\Omega \cdot \text{m})^{-1}$, and 1.513 at 1000 Hz, respectively. The lead zirconate titanate powder produced has potential applications as materials used for actuators, multilayer capacitors, sensors, ultrasonic transducers and electro-optic devices for data storage.

Keywords: Lead zirconate titanate (PZT), Lead glycolate precursor, Sodium tris (glycozirconate) precursor, Titanium glycolate precursor and Piezoelectric materials.

7.2 Introduction

Lead zirconate titanate, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) of the ABO_3 perovskite structure, was discovered as a piezoelectric material in the 1950s. Since then, it has been identified as an important ferroelectric material suitable for a variety of applications: high energy capacitors, nonvolatile memories, ultrasonic sensors, infrared detectors, and electrooptic devices [1,2,3]. It may exist as the single phase mixed compound of ferroelectric PbTiO_3 (Curie temperature $T_C = 490^\circ\text{C}$) or the antiferroelectric PbZrO_3 ($T_C = 230^\circ\text{C}$) in the isomorphous $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, where $x < 1$. The phase diagram, as proposed by Jaffe *et al.* [4] and still well recognized, reveals the existence of the nearly temperature-independent morphotropic phase boundary MPB at $x \sim 0.5$. The MPB separates the rhombohedral Zr-riched phase from the tetragonal Ti-riched phase. The dielectric constant, piezoelectric constant and electromechanical coupling coefficient all show pronounced maximum values for the composition corresponding to the MPB [5,6].

Several conventional PZT synthesis methods usually involve high calcination temperature to produce the perovskite phase. The calcination usually inevitably leads to PZT particle coarsening and aggregation, and consequently nonuniform microstructure and poor electrical properties of PZT. To alleviate this problem, wet-chemistry-based processes were chosen to prepare PZT powders at lower temperature than the solid-state reaction process. The chemical processes include the co-precipitation, the sol-gel process, and the hydrothermal process. Among these methods, the sol-gel process has been widely viewed as a promising one because of the product uniformity at the molecular level and its low operating temperature. However, the sol-gel process has several disadvantages when employed to prepare PZT ceramics in large quantity; the sol-gel process requires a great deal of solvents and it is very time consuming [7]. Mandel *et al.* (2003) synthesized $\text{PbZr}_{0.7}\text{Ti}_{0.3}\text{O}_3$ nanoparticles possessing a new tetragonal crystal structure with a polymeric precursor and polyvinyl alcohol [1]. Zhang *et al.* (2002) prepared PZT ceramics derived from a hybrid method between the sol-gel process and the solid-state reaction. Reaction of the oxides to PZT occurred at a temperature as low as 500°C , which is believed to be induced by the PZT crystallized from the sol-gel portion in the system. Junmin *et al.* (2000) synthesized lead zirconate titanate from an

amorphous precursor by mechanical activation. The resulting PZT powder was well dispersed and the particle size was in the range of 30-50 nm, as observed by SEM and TEM. The dielectric constant measured at 1kHz. was as high as 9100 along with the Curie temperature of 380°C for PZT sintered at 1150°C for 1 h and mechanically activated for 20 h [3].

From these previous studies, the sol-gel process appears as an alternative method to produce lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, (PZT) of ABO_3 perovskite structure from lead, titanium, and zirconium (IV) alkoxide precursors, although these precursors are moisture sensitive. Wongkasemjit *et al.* [8-10] have demonstrated that using the Oxide One Pot Synthesis (OOPS) process, moisture stable metal alkoxides can be successfully synthesized. Therefore, the objective of our study is to synthesize high purity lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, (PZT) via the sol-gel process using lead glycolate [10], titanium glycolate [9], and sodium tris (glycozirconate) [8], as the moisture stable precursors. In our work, PZT sols were prepared by mixing lead glycolate, titanium glycolate, and sodium tris(glycozirconate) at Pb:Zr:Ti mole ratios of 1:0.2:0.8; 1:0.3:0.7; 1:0.4:0.6; 1:0.5:0.5; 1:0.6:0.4; 1:0.7:0.3; 1:0.8:0.2. The mixtures were then dried and calcined to form PZT powders. We investigated the influences of calcination temperature and time on morphology, electrical properties, and the phase transformation.

7.3 Experimental

Materials

The starting raw materials were lead glycolate, titanium glycolate, and sodium tris (glycozirconate) as required by the oxide one pot synthesis process (OOPS) [8-10] which yields less moisture sensitive products.

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). Titanium dioxide was purchased from Sigma-Aldrich Chemical Co., Ltd. (USA). Zirconium (IV) hydroxide $\text{Zr}(\text{OH})_4$ containing 88.8% ZrO_2 purity was purchased from Sigma-Aldrich Chemical Co., Ltd. (USA). Sodium hydroxide

NaOH of 98% purity was obtained from Asia Pacific Specialty Chemicals Inc. Limited, and used as received. Ethylene glycol (EG) was purchased from Farmitalia Carlo Erba (Barcelona) or Malinckrodt Baker, Inc. (USA), and purified by a fractional distillation under nitrogen at atmosphere pressure, 200°C before use. Triethylenetetramine (TETA) was purchased from Facai Polytech. Co.,Ltd. (Thailand) and distilled under vacuum (0.1 mm/Hg) at 130°C prior to use. Acetonitrile, HPLC grade, was purchased from Lab-Scan Co., Ltd.

Instrumental

The positive fast atom bombardment mass spectra (Maldi-tof-MS) were recorded on a Bruker Instrument (Bruker, Polymer TOF) using sinapinic acid as a matrix, a cesium gun as indicator, and cesium iodide (CsI) as a standard for peak calibration. An elemental analyzer was used to determine CHNS/O compositions (Perkin Elmer, PE 2400 Series II) through pyrolysis. Fourier transform infrared spectra (FTIR) were obtained from a spectrometer (Bruker, Vector 3.0) with a spectral resolution of 4 cm⁻¹. A thermal gravimetric analysis (TGA) and a differential thermal analysis (DTA) were carried out using a thermal analyzer (Perkin Elmer, TGA 7) with a heating rate of 10°C/min over a 25°-1200°C temperature range. The Raman spectra of powder samples were obtained using a spectrometer (Labram HR 800, DU-420-OE-322). X-ray diffraction patterns (XRD) were taken and analyzed using an X-ray analyzer (Philips, N.V. 1999) consisting of CuK α radiation ($\lambda = 0.154$ nm). Micrographs were obtained using a scanning electron microscope (JEOL, 5200) equipped with EDS for X-ray microanalysis. The percentages of chemical compositions of calcined samples were obtained by an X-ray analytical microscope (Horiba, XGT 2000w). Electrical properties were measured using an impedance analyzer (HP, 4284A).

Starting Material Preparation

Lead Glycolate

Lead glycolate was synthesized via the OOPS process [10]. A mixture of lead acetate trihydrate (Pb(CH₃COO)₂·3H₂O, 0.1 mol, 37.9 g), ethylene glycol (EG, 0.1 mol, added excess 50 cm³) and triethylenetetramine (TETA, 0.1 mol, 14.6 g) acting as a catalyst was heated at the boiling point of EG under N₂ atmosphere in a

thermostatted oil bath. The excess EG was slowly distilled off as to remove water liberated from the reaction. After heating at 200°C for 1 h, the solution color changed to yellow or golden brown. The reaction mixture was cooled to obtain a crude precipitate product followed by a filtration with acetonitrile. The light bronze solid product was obtained and dried in a vacuum dessicator (0.1 mm Hg) at room temperature.

FTIR: peaks at 2778-2829 cm^{-1} ($\nu\text{C-H}$), 1086, 1042 cm^{-1} ($\nu\text{C-O-Pb}$ bond), and 573 cm^{-1} ($\nu\text{Pb-O}$ bond) were observed as shown in Fig. 7.1. ^{13}C -solid state NMR: only one single peak at 68.6 ppm appeared due to $\text{CH}_2\text{-OH}$ of EG. From the EA analysis, we found 8.864% for C and 1.392% for H, comparable to the calculated values of 8.990% for C and 1.498% for H. From the FAB^+ -MS analysis, we obtained approximately 55% of the highest m/e at 801 for $[-(\text{-PbOCH}_2\text{CH}_2\text{O-})_3^-]$, 25% intensity at 595 for $[-\text{OCH}_2\text{CH}_2\text{OPbOCH}_2\text{CH}_2\text{OPbOCH}_2\text{CH}_2\text{O-}+\text{H}^+]$ and 56% intensity at m/e 505 for $[-\text{CH}_2\text{OPbOCH}_2\text{CH}_2\text{OPb-}+\text{H}^+]$. From the DSC-TGA analysis, a decomposition occurred at 290°-305°C, with a 82.5% ceramic yield ($-\text{PbOCH}_2\text{CH}_2\text{O-})_3$.

Sodium tris (glycozirconate)

Sodium tris (glycozirconate) was also synthesized via the OOPS process [8]. A mixture of zirconium hydroxide (Zr(OH)_4 , 11.4 m mol, 1.59 g) and 200 mol% sodium hydroxide NaOH equivalent to zirconium hydroxide were suspended in 35 ml of ethylene glycol. The reaction mixture was heated under nitrogen N_2 atmosphere in a thermostatted oil bath for 12 h.

FTIR: peaks at 2939-2873 cm^{-1} ($\nu\text{C-H}$) and 1090 cm^{-1} ($\nu\text{C-O-Zr}$ bond) were observed as shown in Fig.7.1. The peaks between 1400-1200 cm^{-1} can be attributed to the C-H vibrations of the methylene group. Sodium tris (glycozirconate) complex displayed the peak at 1090 cm^{-1} corresponding to the Zr-O-C stretching vibration mode, and the peak of 880 cm^{-1} due to the deformation vibration of the C-C bond. An additional peak occurring at around 613 cm^{-1} can be assigned to the Zr-O stretching frequency [8]. The TGA-DSC profile of sodium tris (glycozirconate) complex has one major thermal decomposition between 350°C and 545°C. Its weight loss of 41.59% corresponds to conversion of as-synthesized product into carbon-free

inorganic materials or to the decomposition of all organic ligands in the product framework. The experimental weight loss of 41.59% is close to and consistent with the expected weight loss calculated for the formation of the proposed product of $\text{Na}_2\text{O}\cdot\text{ZrO}_2$ of 41.67%. The percentage ceramic yield of the product was 58.41%, in good agreement with the calculated value (58.33%). In addition, EDS was used to confirm the formation of $\text{Na}_2\text{O}\cdot\text{ZrO}_2$ after thermal decomposition. The resulting Na/Zr ratio was equal to 1.98, consistent with the proposed oxide product (2.0). The exothermic peak occurred at 430°C. The ^{13}C NMR spectra displayed a single peak at 62.6 belonging to the symmetrical carbon of chelated glycolate ligand $\text{CH}_2\text{-O-Zr}$. Through the elemental analyzer, we found that the obtained percentages of carbon and hydrogen were very close to the theoretically calculated values. For the sodium tris(glycozirconate) precursor, the analytically calculated values are: C = 22.70%; H = 3.78%. We found experimental values of C = 22.41% and H = 4.23%. The MS spectrum fragmentation patterns can be employed on the basis of the proposed structure at m/e values of 635 (11.5% intensity), 297 (87.6% intensity), 182 (100% intensity), and 151 (80.7% intensity) [8].

Titanium glycolate

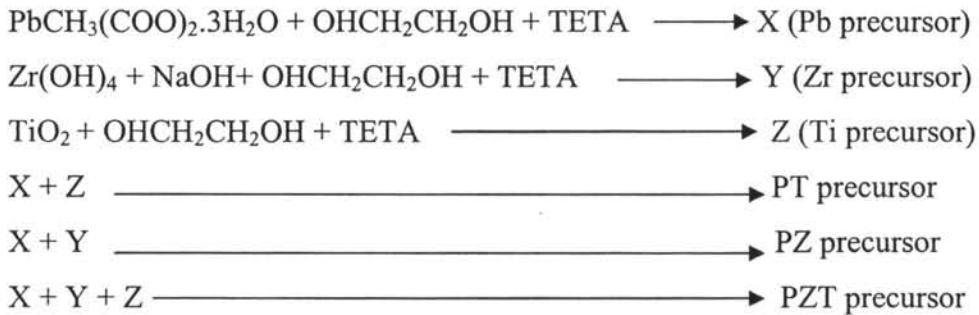
Titanium glycolate was synthesized via the OOPS process as well [9]. A mixture of titanium dioxide (TiO_2 , 0.025 mol, 2 g) and TETA (0.0074 mol, 3.65 g) mixed with ethylene glycol (EG added excess 25 cm^3) was stirred vigorously and heated at the boiling point of EG under N_2 atmosphere. After 24 h, the solution was centrifuged to separate unreacted TiO_2 from the solution part. The excess EG and TETA were removed by a vacuum distillation to obtain a crude precipitate. The white solid product was washed with acetonitrile and dried in a vacuum dessicator.

FTIR: peaks at 2927-2855 cm^{-1} ($\nu\text{C-H}$), 1080 cm^{-1} ($\nu\text{C-O-Ti}$ bond), and 619 cm^{-1} ($\nu\text{Ti-O}$ bond) were observed. ^{13}C -solid state NMR: two peaks at 74.8 and 79.2 ppm were found identifying the titanium-ethyleneglycol ligand bridge bonding [9]. From the EA analysis, we obtained the weights of C at 28.6% and H at 4.8%. The data from FAB^+ -MS indicate that 8.5% intensity at m/e of 169 belongs to $[\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2]\text{H}^+$, 73% intensity at m/e equal to 94 belongs to $[\text{OTiOCH}_2]$, and 63.5% intensity at m/e equal to 45 belongs to $[\text{CH}_2\text{CH}_2\text{OH}]$ [9]. From TGA data, one

sharp transition occurred at 340°C, with corresponding 46.95% ceramic yield of $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ was obtained.

Sol-gel Preparation of Lead Zirconate Titanate

The sol-complex alkoxide mixture was prepared by mixing lead glycolate in a 0.1 M nitric solution (HNO_3) with titanium glycolate and sodium tris (glycozirconate) with the Pb:Zr:Ti mole ratios of PZT 1 (1:0.2:0.8); PZT 2 (1:0.3:0.7); PZT 3 (1:0.4:0.6); PZT 4 (1:0.5:0.5); PZT 5 (1:0.6:0.4); PZT 6 (1:0.7:0.3); and PZT 7 (1:0.8:0.2). White turbid solutions were obtained. The sol to gel transition occurred within a few seconds when a small amount of water was added to adjust pH to be in the range of 9-10 at room temperature. The gels were allowed to settle at room temperature and kept at 50°C for 2 days to finally obtain a light yellow gel. The gels were then calcined at 200°, 300°, 400°, 500°, 600°, 700°, and 800°C for durations of 1, 2 and 3 h. The following six equations summarize our work in the synthesis and the preparations of PT, PZ, and PZT ceramics:



Electrical Properties Characterization

The samples were prepared according to the ASTM B263-94 standard for electrical property measurements. Pellet samples were prepared as a thin disc having 12 mm in diameter and 0.50 mm in thickness. In our experiment, the electrical properties, the dielectric constant, tan delta and electrical conductivity were measured in the frequency range between 10^3 - 10^6 Hz and at room temperature [6, 11-12].

7.4 Results and Discussion

Characterization of Lead Zirconate Titanate Gel and Calcined Lead Zirconate Titanate

FTIR spectra of lead zirconate titanate dried gel (PZT4), lead glycolate, and sodium tris(glycozirconate) precursor are shown in Fig.7.1. For the PZT4 spectrum, there are a visible broad peak at 3500 cm^{-1} ($\nu\text{O-H}$) [2], smaller peaks at 1725 , and 1630 cm^{-1} ($\nu\text{C-O}$), and a peak at 1085 cm^{-1} ($\nu\text{C-O-Pb}$) [13-14]. The broad peak at 783 cm^{-1} can be identified as the Pb-O-Zr stretching [2, 13, 14]. Figure 7.2 shows FTIR spectra of lead zirconate titanate dried gels of various mole ratios between lead glycolate, sodium tris (glycozirconate), and titanium glycolate precursors ((PZT1) 1:0.2:0.8; (PZT2) 1:0.3:0.7; (PZT3) 1:0.4:0.6; (PZT4) 1:0.5:0.5; (PZT5) 1:0.6:0.4; (PZT6) 1:0.7:0.3; and (PZT7) 1:0.8:0.2). The absorbance peaks of PZT's can be observed and are similar to those of PZT4 as shown in Fig.7.2. It may be noted that the peaks at $3,500\text{ cm}^{-1}$ ($\nu\text{O-H}$) [2] and 1630 cm^{-1} ($\nu\text{C-O}$) [13,14] increase in intensity with increasing mole ratio between titanium glycolate and sodium tris (glycozirconate).

Raman spectra of lead glycolate precursor, sodium tris (glycozirconate) precursor, titanium glycolate precursor, dried lead zirconate gel, dried lead titanate gel, and dried lead zirconate titanate gel are shown in Fig.7.3. The spectrum of PZT4 shows a broad band indicating its amorphous structure. The spectra of lead titanate and lead zirconate also show broad bands indicating amorphous structures, consistent with those observed previously [18, 19]. Figure 7.4 shows Raman spectra of lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ of various mole ratios at room temperature. The Raman spectra of PZT6 and PZT7, with the highest mole ratios between titanium glycolate and sodium tris (glycozirconate), show distinct peaks at 680 cm^{-1} and 770 cm^{-1} ; they can be identified as the tetragonal structure of lead titanate [20, 21]. Figure 7.5 shows Raman spectra of dried lead zirconate titanate gels (PZT4) of mole ratio of 1:0.5:0.5 at room temperature, and PZT4 at calcination temperatures of 200°C , 300°C , 400°C , 500°C , 600°C , 700°C and 800°C , and at 1 hr. For calcination temperatures between 400°C to 600°C , distinct peaks appear at 200 cm^{-1} , 300 cm^{-1} ,

600 cm^{-1} , and 700 cm^{-1} indicating the PZT perovskite phase developed with the tetragonal structure [20]. For higher calcination temperatures between 700°C to 800°C, there are two peaks at 550 cm^{-1} and 870 cm^{-1} indicating other crystalline structures which can be identified by XRD data.

A thermogram of dried lead zirconate titanate gel, obtained from the TGA-DTA technique, at temperatures between 25°C and 1200°C is shown in Fig.7.6. The weight loss of dried lead zirconate titanate gel was 44.2%; the percentage of ceramic yield obtained was then 55.8%, close to the calculated value of 49.5. The main weight losses occurred at 268°C and 744°C by exothermic reactions. The sharp exothermic peak at 268°C resulted from the heat of vaporization of EG generated from the hydrolysis. The weight loss at 744°C occurred through the PbO massicot formation.

XRD patterns of dried lead zirconate titanate gels $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$: PZT1; PZT2; PZT3; PZT4; PZT5; PZT6; PZT7 at various mole ratios are shown in Fig.7.7. The dominant peaks at $2\theta = 19^\circ$, 38° , and 39° belong to lead nitrate ($\text{Pb}(\text{NO}_3)_2$) and the peaks at $2\theta = 29^\circ$, 39° , and 42° belong to sodium nitrate (nitratine, NaNO_3), in agreement with JCPDS patterns of 36-1462 and 36-1474, respectively. These were products of the sol-gel process with the additions of nitric acid and sodium hydroxide.

XRD patterns of lead zirconate titanate samples calcined at 200°C, 300°C, 400°C, 500°C, 600°C, 700°C, and 800°C and at calcination times of 1, 2 and 3 h are shown in Fig.7.8. For PZT at calcination temperature of 200°C, we obtained a small amount of the tetragonal structure $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$. For PZT at calcination temperature of 300°C at 1, 2 or 3 h, we obtained a mixture between the tetragonal structure and the lead oxide ($\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [Tetragonal]+PbO[Orthorhombic]) For PZT at calcination temperature of 400°C at 1, 2 or 3 h, we obtained in addition the pyrochlore phase ($\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [Tetragonal]+PbO[Orthorhombic]+ $\text{Pb}_2\text{Ti}_2\text{O}_6$). For PZT at calcination temperature of 500°C at 1, 2, and 3 h, we obtained a mixture of the tetragonal structure, the cubic lead titanate structure ($\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [Tetragonal]+ PbTiO_3 [Cubic]) [6]. For PZT at calcination temperatures of 600°C and 700°C at 1, 2 or 3 hr, we obtained the cubic structure and lead oxide ($\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [Cubic]+PbO[Cubic & Orthorhombic]+ PbO_2 [Cubic]). Finally, for

PZT at calcination temperature of 800°C at 1, 2 or 3 h, we obtained the cubic structures $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [Cubic]+ PbO_2 [Cubic]. These peaks in Fig.7.8 are consistent with those of the Joint Committee on Powder Diffraction Standards (JCPDS) patterns of (14-0031), (38-1477), (40-0099), (50-0346), and (26-0142) [2, 6-7].

^{13}C -NMR spectra of lead glycolate, sodium tris (glycozirconate), titanium glycolate, dried lead zirconate gel, dried lead titanate gel, and dried lead zirconate titanate gel are shown in Fig.7.9. All of spectra commonly show the peak of ethylene glycol ligand at 69 ppm, consistent with previously reported data [8-10,14].

The microstructure transformation of our calcined samples can be observed from SEM micrographs at the same magnification 350 as shown in Fig.7.10. Lead zirconate titanate particles became agglomerated starting at 200°C, as shown in Figure 7.10b. Particle shapes are quite irregular and sizes are nonuniform.

The chemical composition percentages of calcined samples were analyzed by an X-ray analytical microscope and data are tabulated as shown in Table 7.1. The experimental mole ratio of $\text{PbO} / \text{ZrO}_2 / \text{TiO}_2$ of 1.00:0.521:0.479 is close to the theoretically calculated mole ratio of the lead zirconate titanate $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ or PZT4, which is 1.00:0.500:0.500. From the elemental analysis, data were used to calculate the percentage of carbon which turns out to be 4.548 ± 0.101 , a value close to theoretically calculated chemical composition of 4.424. From the mass spectroscopy, we obtained a molecular weight of 1085 g/mol for our calcined samples. Based on these data, we proposed the structure as shown in Table 7.2.

Electrical Properties of Synthesized Lead Zirconate

Figures 7.11a and 7.11b show the dielectric constants and dielectric loss tangents of the starting precursors and dried lead zirconate titanate gel as functions of frequency at 27°C. It can be seen that the dried lead titanate gel possesses the highest dielectric constant at 1000 Hz and the highest electric conductivity; namely, 1150 and 2.76×10^{-4} S/m, respectively. The dielectric constants and the dielectric loss tangents of the five materials generally decrease with increasing frequency, indicative of the polarization mechanisms involved: the electronic, atomic, dipole, and interfacial polarizations [15].

Figures 7.12a and 7.12b show the dielectric constants and the dielectric loss tangents of dried lead zirconate titanate gels $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$: PZT1; PZT2; PZT3; PZT4; PZT5; PZT6; and PZT7 as functions of frequency. Of various mole ratios of Pb:Zr:Ti of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ or PZT4 possesses the highest dielectric constant at all frequencies investigated: from 10^{+3} to 10^{+6} Hz. In addition, the dried lead zirconate titanate gel $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ or PZT4 also possesses the highest dielectric loss tangent values in the same frequency range. Table 7.3 lists dielectric constant, dielectric loss tangent and electrical conductivity values at 10^{+3} Hz at 27°C of the three precursors and the dried lead zirconate titanate gels. At 10^3 Hz, dried PZT4 gel possesses dielectric constant and dielectric loss tangent values of 9.832 and 0.405, respectively.

Table 7.3 also lists dielectric constant, dielectric loss tangent and electrical conductivity values at 1000 Hz and at 27°C of our calcined lead zirconate samples $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ of various calcination temperatures and times. Among these samples, it can be seen that $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ 400_1h, lead zirconate titanate calcined at 400°C for a duration of 1h, possesses the highest dielectric constant of 10190, with corresponding dielectric loss tangent of 1.513, and the highest DC electrical conductivity of 0.803×10^{-3} S/m. This calcined sample corresponds to the most pure tetragonal structure of the perovskite phase along with a small amount of pyrochlore phase, as shown previously from the X-ray data of Fig.7.8. With the tetragonal structure of the perovskite phase, we may expect ferroelectric and piezoelectric properties [16]. At higher calcination temperatures, above the Curie temperature of $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ of 400°C , we may expect both the dielectric constant and the electrical conductivity to decrease with increasing calcination temperature since the structures become more of the cubic form, which is accompanied by paraelectricity [16].

Figures 7.13a and 7.13b show the dielectric constants and the dielectric loss tangents of lead zirconate titanate samples $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ or PZT4 of various frequencies at functions of calcination temperature. For the sample PZT4, its dielectric constant and dielectric loss tangent increase initially with calcination temperature and reach maximum values at 400°C and then decrease at higher calcination temperature. The maximum dielectric constant and dielectric loss values

obtained are 10190 and 1.513, respectively as expected to occur close to the Curie temperature of 400°C. We may compare our data of our synthesized $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ or PZT4 with the data of other previous workers who obtained dielectric constant of 8600 [17] and 1050 [7], measured at 1000 Hz. and at room temperature.

7.5 Conclusions

Our synthesis of lead zirconate titanate by the sol-gel process using lead glycolate, sodium tris (glycozirconate) and titanium glycolate as starting precursors gave high purity and low moisture sensitivity light yellow color powder. The experimental stoichiometry value between PbO , ZrO_2 and TiO_2 is 1.00:0.521:0.479, close to the calculated value of PbZrO_3 . The lead zirconate titanate gel was dried and calcined below the Curie temperature T_c in order to prevent the structural change from the tetragonal or the orthorhombic forms to the cubic form in the perovskite phase. The highest dielectric constant of 10190, electrical conductivity of $0.803 \times 10^{-3} (\Omega \cdot \text{m})^{-1}$, and low dielectric loss tangent of 1.513 measured at 1000 Hz. were obtained with $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ calcined at 400°C for 1 h. Dielectric constant and conductivity decreased with calcination time and temperature when it was above the Curie temperature T_c . Our synthesized materials appear to be a suitable candidate for using as an electronic-grade $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$.

7.6 Acknowledgements

The authors would like to thank Postgraduate Education and Research Program in Petroleum and Petrochemical Technology (ADB) Fund, Ratchadapisake Sompoch Fund, Chulalongkorn University and the Faculty of Engineering, Kasetsart University for the grant support, and Department of Materials Engineering, Chemical Department and Physical Department, Kasetsart University, for x-ray diffraction, and electrical property measurements.

7.7 References

- [1]. T. K. Mandal, S. Ram, *Mat.Lett.* 57(2003) 2432.
- [2]. R. Tipakontitikul, S. Ananta, *Mat.Lett.* 58(2004) 449.
- [3]. X. Junmin, J. Wang, T. Weiseng, *J. All. Com.* 308(2000) 139.
- [4]. B. Jaffe, R. S. Roth, S. Marzullo, *J.Appl. Phys.* 25(1954) 809.
- [5]. S. K. Misra, A. P. Singh, D. Pandey, *P. Mag, Philos. Mag.* B76(1997) 213.
- [6]. L. B. Kong, J.Ma, *Mat. Lett.*, 51(2001) 95.
- [7]. R. F. Zhang, J.Ma, L.B.Kong, Y.Z.Chen, T.S.Zhang, *Mat.Lett.* 55(2002) 388.
- [8]. B. Ksapabutr, E.Gulari, and S. Wongkasemjit, *Mater. Chem. Phys.* 83/1(2004) 34.
- [9]. N. Phonthammachai, T. Chairassameewong, E. Gulari, A. Jamieson, S. Wongkasemjit, *J. Metals. Min. Mater., Chulalongkorn University*, 12/1(2002) 23.
- [10]. N. Tangboriboon, A. Jamieson, A. Sirivat, and S. Wongkasemjit, *Excellent Electrical Properties of a Novel Lead Alkoxide Precursor: Lead glycolate* *Mater. Chem. Phys.*98 (2006) 138-143.
- [11]. R. Thomas, S. Mochizuki, T. Mihara, T. Ishida, *Mat. Lett.*, 57(2003) 2007.
- [12]. W. C. Las, P. D. Spagnol, M. A. Zaghete, M. Cilense, *Cer. Int.*, 27(2001) 367.
- [13]. A. Abreu Jr., S. M. Zanetti, M. A. S. Oliveira, G. P. Thin, *J. Eur. Soc.*, 25(2005) 743.
- [14]. M. Kakihana, T. Okubu, M. Arima, O. Uchiyama, M. Yashima, M. Yuchimura, *Chem. Mater.*, 9/2(1997) 451.
- [15]. S. S. N. Bharadwaja, S. B. Krupanidhi, *Thin Solid Films*, 391(2001) 126.
- [16]. A.S. Deshpande, Y.B. Khollam, A.J. Patil, S.B. Deshpande, H.S. Potdar, S.K. Date, *Mat. Lett.*, 51(2001) 161.
- [17]. Z. J. Xu, R. Q. Chu, G. R. Li, X. Shao, Q. R. Yin, *Mat. Sci.Eng.*, Bxxx (2004) xxx (Article in press).
- [18]. D. Bersani, P.P. Lottici, A. Montenero, S. Pigoni, G. Gnappi, *J. Crys, Solid.*, 192-193 (1995) 490.
- [19]. E. R. Camargo, M. Popa, J. Frantti, and M. Kakihana, *Chem. Mater.*, 13 (2001) 3943.

- [20]. F. M. Pontes, E.R. Leite, M.S.J. Nunes, D.S.L. Pontes, E. Longo, R. Magnani, P.S. Pizani, J.A. Varela, *J. Eur. Cer. Soc.*, 24 (2004) 2969.
- [21]. G. Burns and B. A. Scott, *Phys. Rev. Lett.*, 25/17 (1970) 1191.

Captions of Figures and Tables

- Figure 7.1 FTIR spectra: lead glycolate precursor; titanium glycolate precursor; sodium tris (glycozirconate) precursor, dried PbTiO_3 gel, dried PbZrO_3 gel, and dried lead zirconate titanate PZT4 gel.
- Figure 7.2 FTIR spectra of the dried lead zirconate titanate gels at various mole ratios Pb:Zr:Ti: PZT 1 (1:0.2:0.8); PZT 2 (1:0.3:0.7); PZT 3 (1:0.4:0.6); PZT 4 (1:0.5:0.5); PZT 5 (1:0.6:0.4); PZT 6 (1:0.7:0.3); PZT 7 (1:0.8:0.2).
- Figure 7.3 Raman spectra of lead glycolate precursor; sodium tris (glycozirconate) precursor; titanium glycolate precursor; dried PbZrO_3 gel; dried PbTiO_3 gel, and dried PZT4 gel.
- Figure 7.4 Raman spectra of PZT1; PZT2; PZT3; PZT4; PZT5; PZT6; PZT7.
- Figure 7.5 Raman spectra of dried lead zirconate titanate PZT4 gel, and calcined lead zirconate titanates at 200°C; 300°C; 400°C; 500°C; 600°C; 700°C; 800°C for 1h.
- Figure 7.6 TGA-DSC thermograms of dried lead zirconate titanate PZT4 gel from 25°C to 1200°C.
- Figure 7.7 XRD diffraction patterns of dried irconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ gels: PZT1; PZT2; PZT3; PZT4; PZT5; PZT6; PZT7.
- Figure 7.8 XRD diffraction patterns of calcined lead zirconate titanate powders (PZT4) at 200°C; 300°C; 400°C; 500°C; 600°C; 700°C; 800°C for durations of 1, 2, and 3 h.
- Figure 7.9 ^{13}C -Solid state NMR spectra of the synthesized lead glycolate precursor, sodium tris(glycozirconat) precursor, titanium glycolate precursor, dried PbZrO_3 gel, dried PbTiO_3 gel, and dried PZT4 gel.
- Figure 7.10 SEM micrographs showing microstructure of dried PZT4 gel and calcined PZT4 at: a) 25°; b) 200°C; c) 300°C; d) 400°C; e).500°C; f) 600°C; g) 700°C; and h) 800°C for 1 h at the magnification of 350.
- Figure 7.11 Dielectric constant and tan delta of lead glycolate precursor, sodium tris(glycozirconate) precursor, dried lead zirconate gel, dried lead

titanate gel, and dried lead zirconate titanate (PZT4) gel vs. frequency measured at room temperature.

- Figure 7.12 Dielectric constant and tan delta of dried lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ gels: PZT1; PZT2; PZT3; PZT4; PZT5; PZT6; PZT7 vs. frequency measured at room temperature.
- Figure 7.13 Dielectric constant and tan delta of calcined lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT4) vs. calcination temperature (200°C, 300°C, 400°C, 500°C, 600°C, 700°C and 800°C) for 1h. at various frequencies.
- Table 7.1 The percentages of PbO , ZrO_2 , and TiO_2 in dried lead zirconate titanate gels: PZT1; PZT2; PZT3; PZT4; PZT5; PZT6; PZT7 and calcined lead zirconate titanate PZT4 $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ of various calcination temperatures with corresponding Pb:Zr:Ti mole ratios.
- Table 7.2 The proposed structure and the percentage of carbon content in dried lead zirconate titanate PZT4 gel.
- Table 7.3 The dielectric properties (1000 Hz, 27°C) and DC electrical conductivity of lead glycolate precursor, sodium tris (glycozirconate) precursor, titanium glycolate precursor, dried lead zirconate titanate of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ gels: PZT1; PZT2; PZT3; PZT4; PZT5; PZT6; PZT7 and calcined lead zirconate titanate PZT4 of various calcination temperatures.

Table 7.1 The percentages of PbO, ZrO₂, and TiO₂ in dried lead zirconate titanate gels: PZT1; PZT2; PZT3; PZT4; PZT5; PZT6; PZT7 and calcined lead zirconate titanate PZT4 Pb(Zr_xTi_{1-x})O₃ of various calcination temperatures with corresponding Pb:Zr:Ti mole ratios.

Samples: Pb:Zr:Ti	Color	%PbO	%ZrO₂	%TiO₂	Mole ratio Pb:Zr:Ti
PZT1 (1:0.8:0.2)	Light yellow	74.54	22.31	3.15	1:0.822:0.178
PZT2 (1:0.7:0.3)	Light yellow	78.42	17.02	4.56	1:0.708:0.292
PZT3 (1:0.6:0.4)	Light yellow	77.37	15.58	7.05	1:0.587:0.413
PZT4 (1:0.5:0.5)	Light yellow	76.12	13.98	9.90	1:0.479:0.521
PZT5 (1:0.4:0.6)	Light yellow	74.34	13.51	12.15	1:0.420:0.580
PZT6 (1:0.3:0.7)	Light yellow	63.51	16.22	20.27	1:0.342:0.658
PZT7 (1:0.2:0.8)	Light yellow	77.18	7.74	15.07	1:0.250:0.750
PZT4 (200_1h)	Dark brown	71.35	13.76	14.89	1:0.376:0.624
PZT4 (200_2h)	Dark brown	74.57	13.50	11.92	1:0.433:0.576
PZT4 (200_3h)	Dark brown	65.26	22.65	12.09	1:0.549:0.451
PZT4 (300_1h)	Brown yellow	72.86	14.49	12.65	1:0.427:0.573
PZT4 (300_2h)	Brown yellow	68.46	17.39	14.16	1:0.444:0.556
PZT4 (300_3h)	Brown yellow	72.47	17.49	10.04	1:0.531:0.469
PZT4 (400_1h)	Dark yellow	67.83	18.55	13.62	1:0.531:0.469
PZT4 (400_2h)	Dark yellow	70.83	16.78	12.39	1:0.468:0.532
PZT4 (400_3h)	Dark yellow	73.68	15.62	10.70	1:0.487:0.513
PZT4 (500_1h)	Dark yellow	70.14	18.69	11.17	1:0.521:0.479
PZT4 (500_2h)	Dark yellow	73.90	15.67	10.43	1:0.493:0.507
PZT4 (500_3h)	Dark yellow	71.43	16.82	11.74	1:0.482:0.518
PZT4 (600_1h)	Orange yellow	74.89	12.00	13.10	1:0.373:0.627
PZT4 (600_2h)	Orange yellow	73.44	14.01	12.56	1:0.420:0.580
PZT4 (600_3h)	Orange yellow	69.91	15.73	14.36	1:0.416:0.584
PZT4 (700_1h)	Yellow	69.12	19.84	11.05	1:0.539:0.461
PZT4 (700_2h)	Yellow	70.57	11.76	17.67	1:0.302:0.698
PZT4 (700_3h)	Yellow	62.59	19.76	17.66	1:0.421:0.579
PZT4 (800_1h)	Light yellow	55.36	18.14	26.50	1:0.308:0.692
PZT4 (800_2h)	Light yellow	77.06	9.59	13.35	1:0.318:0.682
PZT4 (800_3h)	Light yellow	55.56	14.31	30.13	1:0.236:0.764

Table 7.2 The proposed structure and the percentage of carbon content in dried lead zirconate titanate PZT4 gel.

M/e	Proposed structure	% carbon content (experimental)	% carbon content (calculated chemical composition)
1085	$ \begin{array}{c} \text{OCH}_2\text{CH}_2\text{OH} \quad \quad \quad \text{O} \\ \quad \quad \quad \\ \text{Pb-O-Ti-O-Zr-O-Pb-O-Ti-} + \text{H}^+ \\ \quad \quad \quad \\ \text{O} \quad \quad \quad \text{O} \\ \quad \quad \quad \\ \text{O-Zr-OO-Ti-O} \\ \quad \quad \quad \\ \text{O} \quad \quad \quad \text{O} \\ \text{OCH}_2\text{CH}_2\text{O} \end{array} $	4.548 ⁺ / ₋ 0.101	4.421

Table 7.3 The dielectric properties (1000 Hz, 27°C) and DC electrical conductivity of lead glycolate precursor, sodium tris(glycozirconate) precursor, titanium glycolate precursor, dried lead zirconate titanate of $Pb(Zr_xTi_{1-x})O_3$ gels: PZT1; PZT2; PZT3; PZT4; PZT5; PZT6; PZT7 and calcined lead zirconate titanate PZT4 of various calcination temperatures.

Samples	Dielectric constant	Dielectric loss tangent (tan δ)	Conductivity ($\Omega.m$) ⁻¹
Lead glycolate precursor	691.70	2.481	8.850×10^{-5}
Sodium tris (glycozirconate) precursor	0.0506	0.635	1.781×10^{-8}
Titanium glycolate precursor	15.70	1.831	1.390×10^{-6}
Dried lead titanate gel	1150	4.261	2.76×10^{-4}
Dried lead zirconate gel	73.76	4.448	1.516×10^{-4}
Dried PZT1 gel	4.496	0.354	6.450×10^{-8}
Dried PZT2 gel	4.501	0.084	2.650×10^{-8}
Dried PZT3 gel	3.165	0.236	1.920×10^{-8}
Dried PZT4 gel	9.832	0.405	9.980×10^{-8}
Dried PZT5 gel	6.522	0.232	8.700×10^{-8}
Dried PZT6 gel	4.997	0.419	6.620×10^{-8}
Dried PZT7 gel	6.273	0.163	4.690×10^{-8}
PZT4 (200_1h)	15.49	2.473	3.055×10^{-5}
PZT4 (200_2h)	12.43	2.350	9.210×10^{-5}
PZT4 (200_3h)	429.9	2.588	4.430×10^{-5}
PZT4 (300_1h)	2613	1.437	3.210×10^{-5}
PZT4 (300_2h)	2817	1.232	1.940×10^{-4}
PZT4 (300_3h)	4088	1.356	1.840×10^{-4}
PZT4 (400_1h)	10190	1.513	0.803×10^{-3}
PZT4 (400_2h)	1922.3	1.370	0.646×10^{-4}
PZT4 (400_3h)	1936.0	1.866	1.970×10^{-4}
PZT4 (500_1h)	907.3	2.182	1.050×10^{-4}
PZT4 (500_2h)	602.7	1.507	2.280×10^{-4}
PZT4 (500_3h)	602.5	1.834	0.820×10^{-6}
PZT4 (600_1h)	8.275	1.376	7.040×10^{-6}
PZT4 (600_2h)	0.8987	0.311	1.540×10^{-7}
PZT4 (600_3h)	0.2350	0.552	0.730×10^{-7}
PZT4 (700_1h)	1.3520	0.320	2.360×10^{-7}
PZT4 (700_2h)	1.0820	0.310	1.850×10^{-7}
PZT4 (700_3h)	1.2690	0.315	2.198×10^{-7}
PZT4 (800_1h)	0.5116	0.227	6.410×10^{-8}
PZT4 (800_2h)	0.6769	0.615	0.227×10^{-8}
PZT4 (800_3h)	0.6360	0.456	0.162×10^{-8}

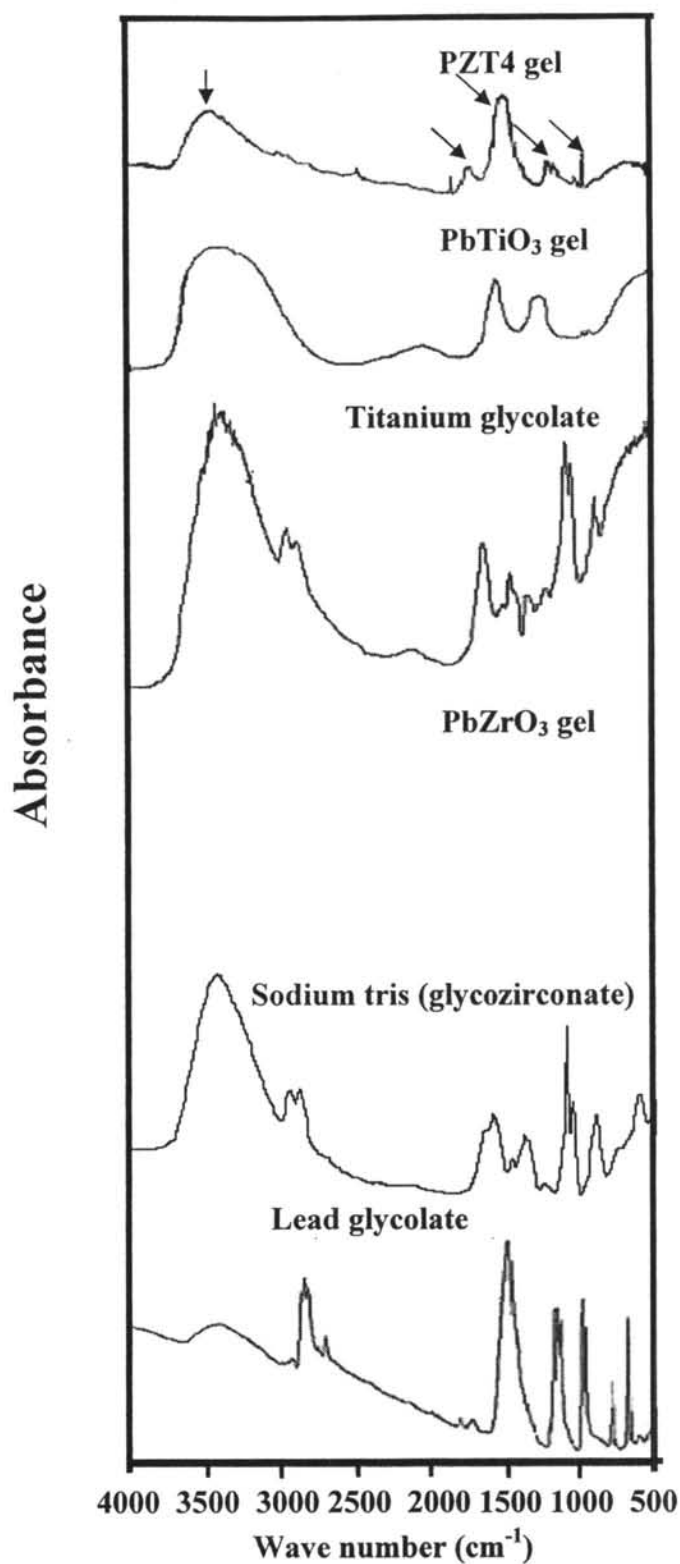


Figure 7.1 FTIR spectra: lead glycolate precursor; titanium glycolate precursor; sodium tris (glycozirconate) precursor, dried PbTiO₃ gel, dried PbZrO₃ gel, and dried lead zirconate titanate PZT4 gel.

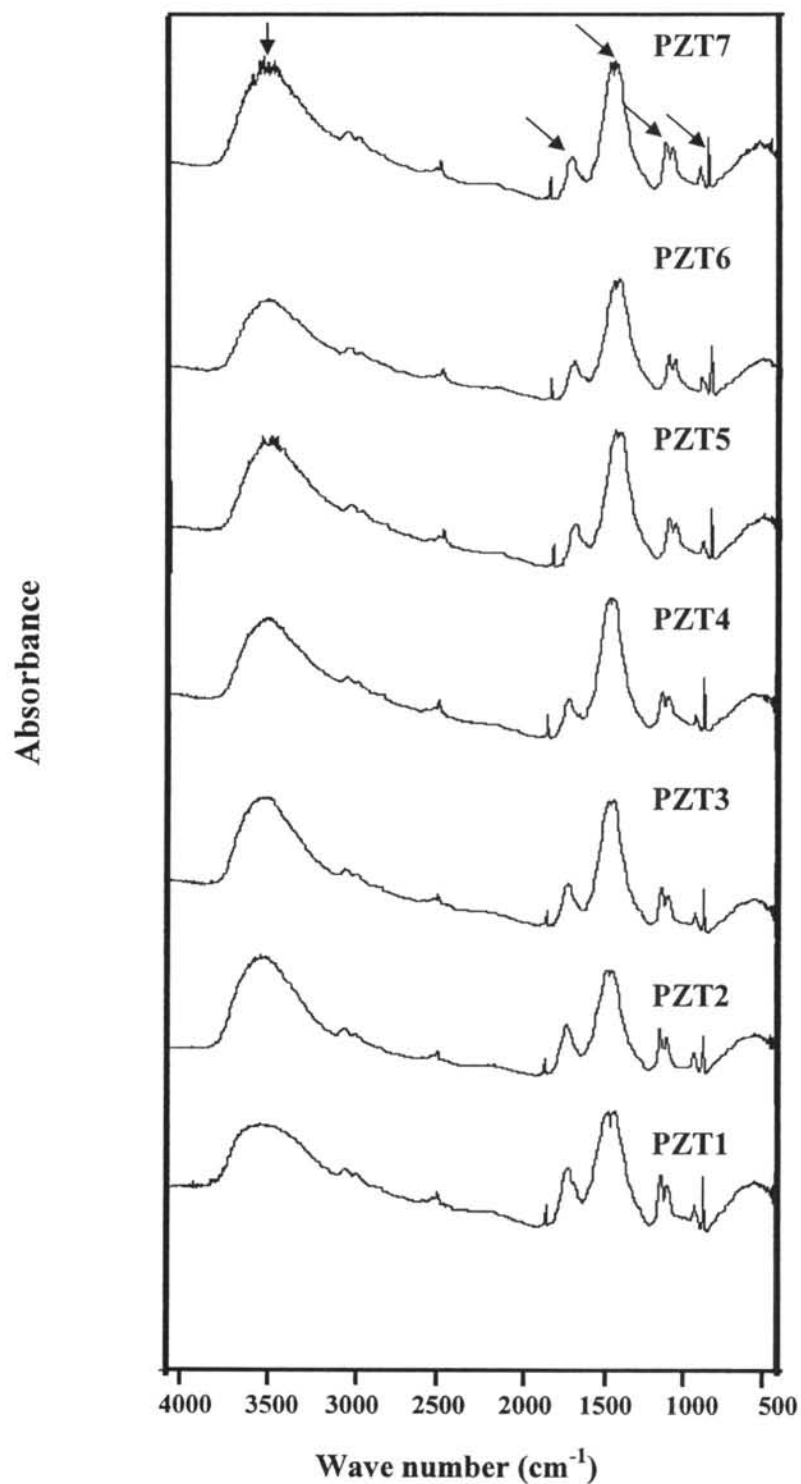


Figure 7.2 FTIR spectra of the dried lead zirconate titanate gels at various mole ratios Pb : Zr : Ti : PZT 1 (1:0.2:0.8); PZT 2 (1:0.3:0.7); PZT 3 (1:0.4:0.6); PZT 4 (1:0.5:0.5); PZT 5 (1:0.6:0.4); PZT 6 (1:0.7:0.3); PZT 7 (1:0.8:0.2).

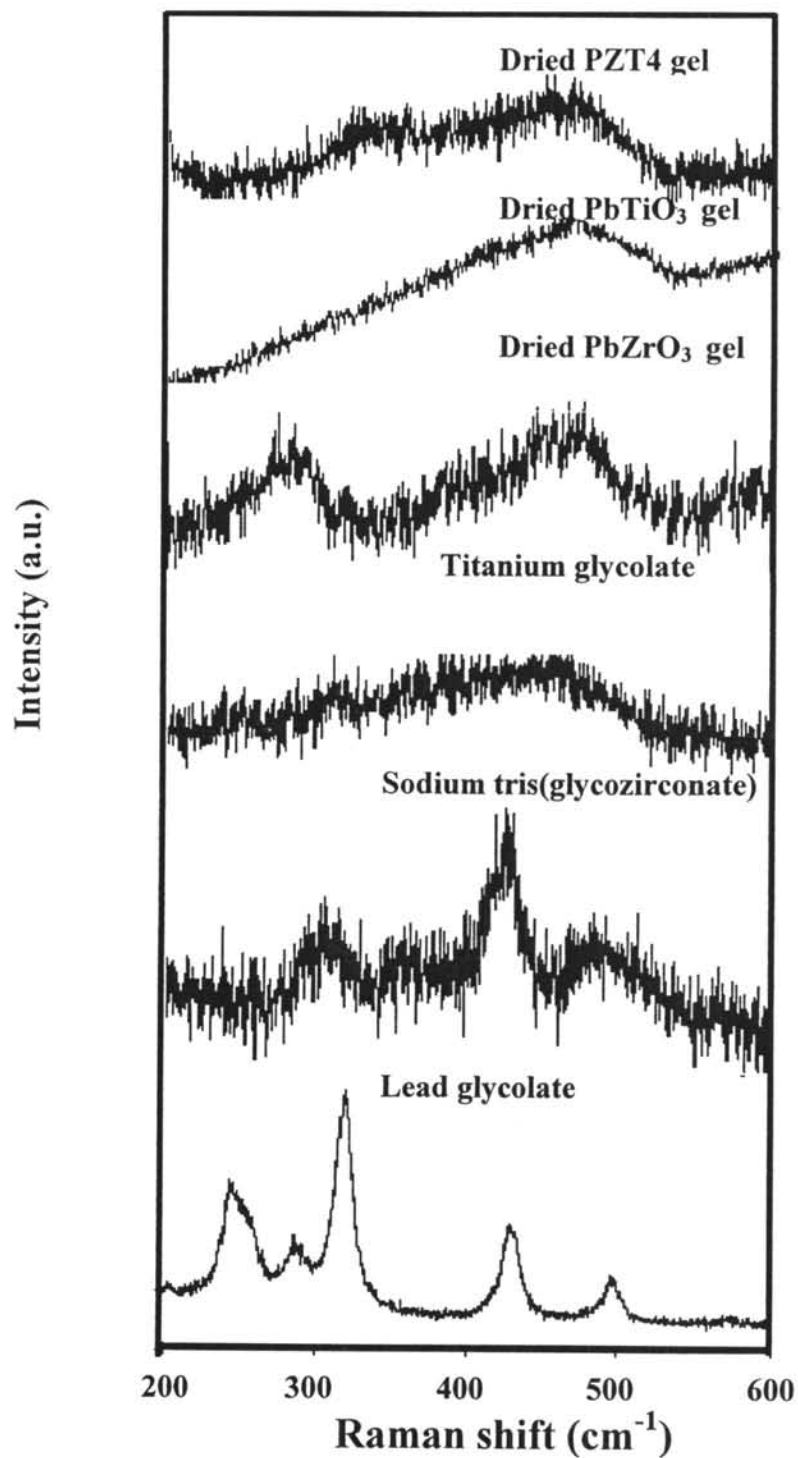


Figure 7.3 Raman spectra of lead glycolate precursor; sodium tris (glyco zirconate) precursor; titanium glycolate precursor; dried PbZrO₃ gel; dried PbTiO₃ gel, and dried PZT4 gel.

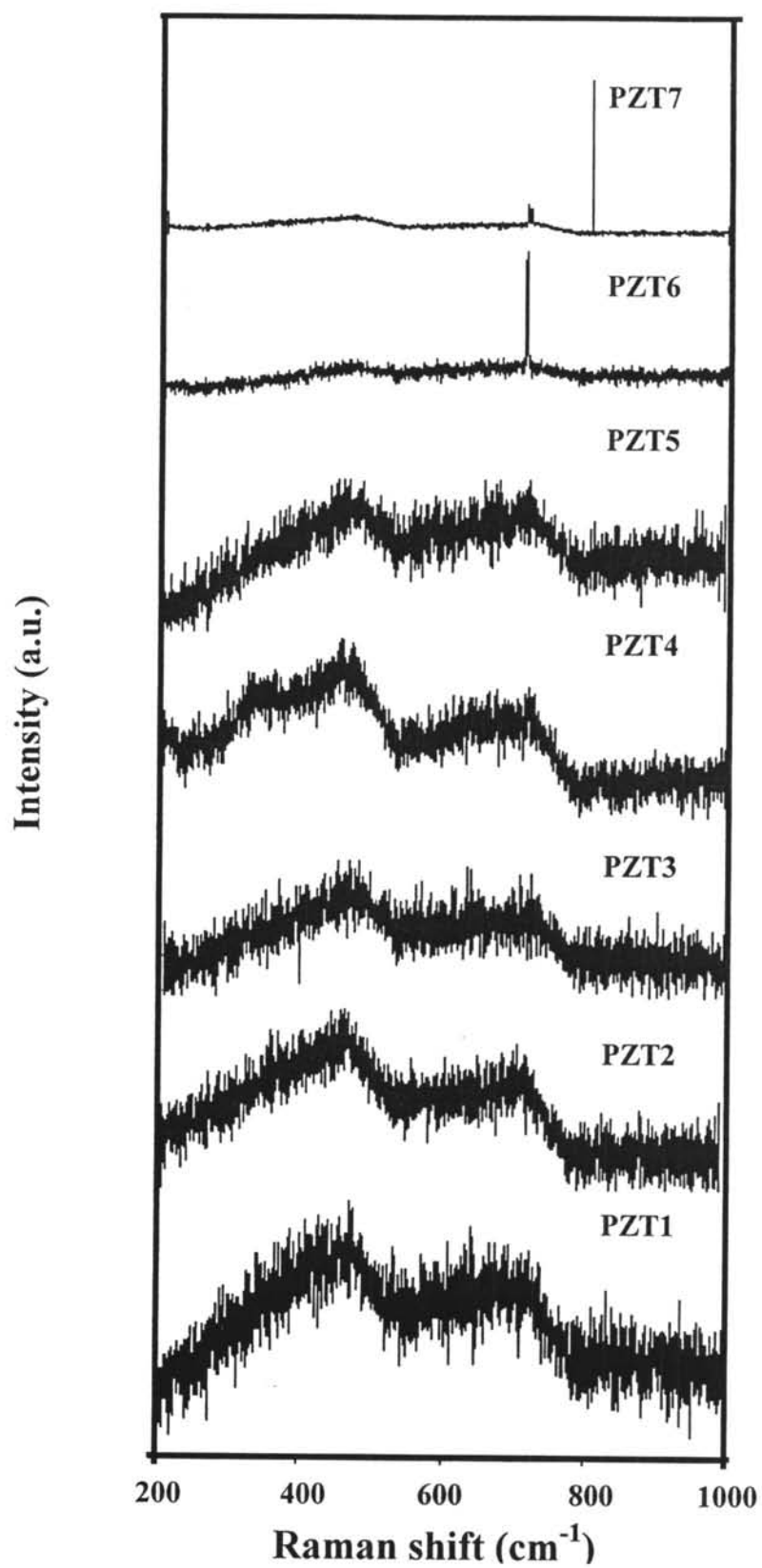


Figure 7.4 Raman spectra of PZT1; PZT2; PZT3; PZT4; PZT5; PZT6; PZT7.

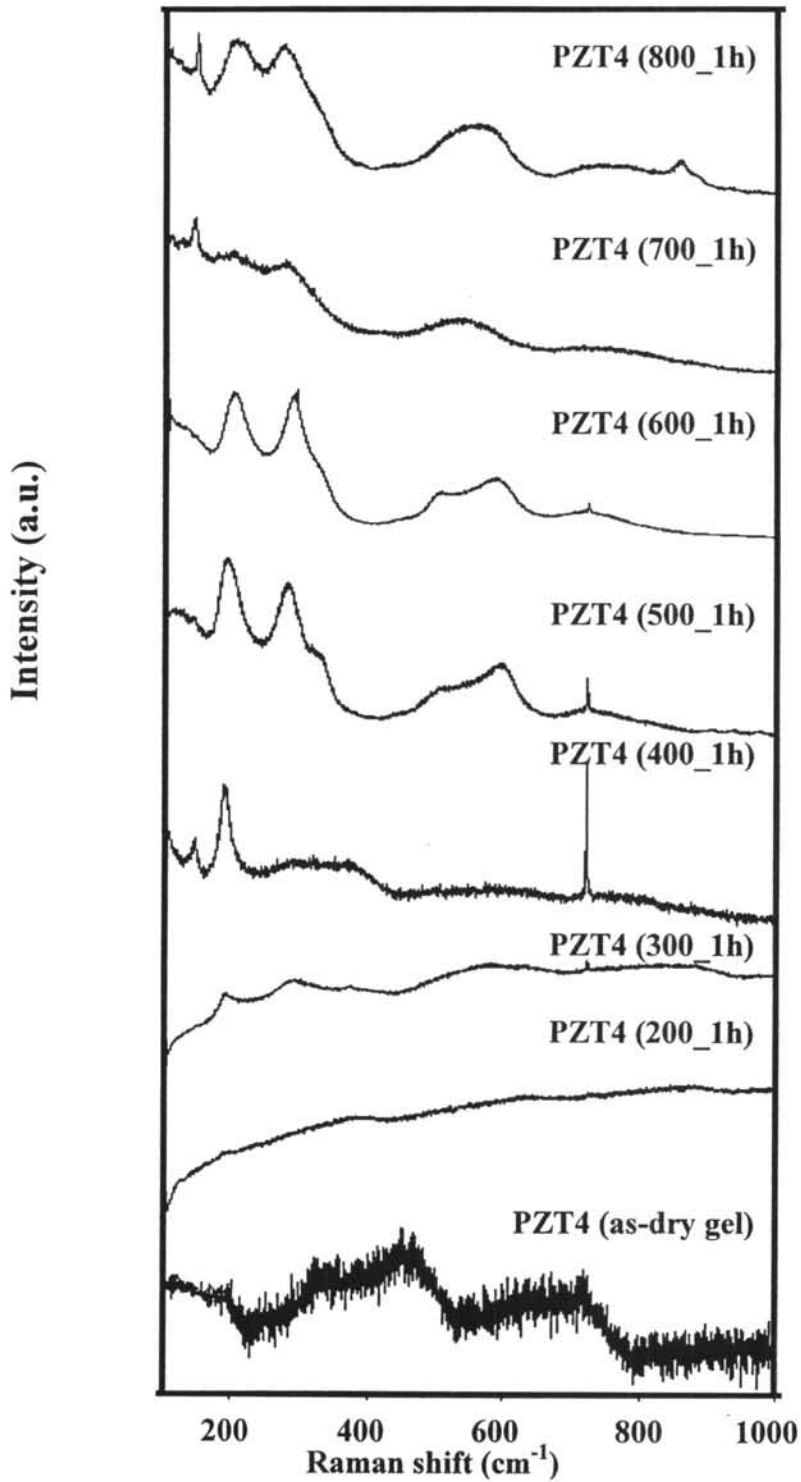


Figure 7.5 Raman spectra of dried lead zirconate titanate PZT4 gel, and calcined lead zirconate titanates at 200° C; 300° C; 400° C; 500° C; 600° C; 700° C; 800° C for 1h.

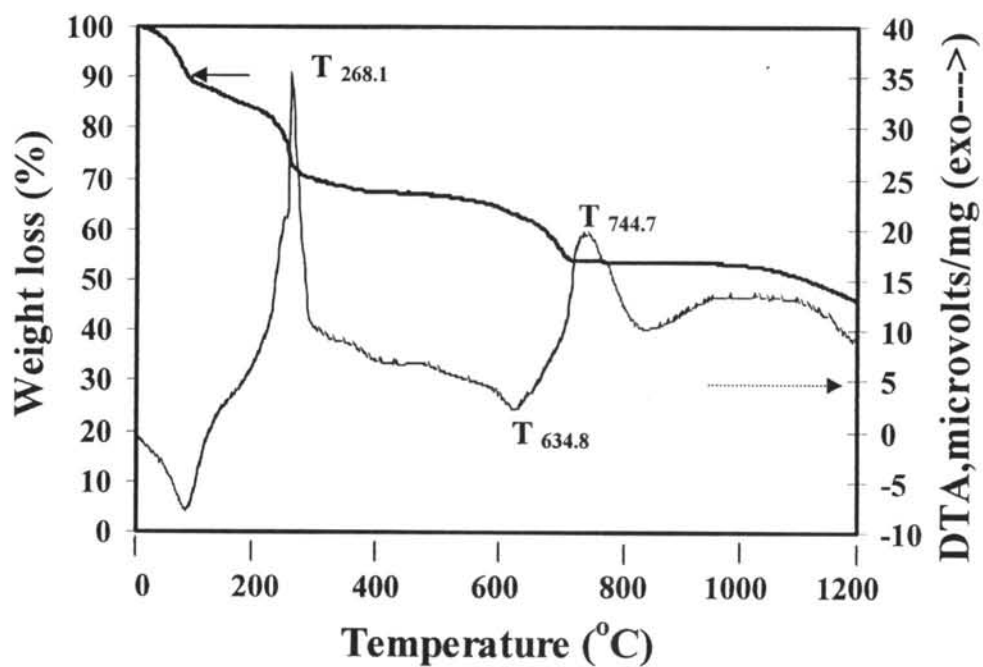


Figure 7.6 TGA-DSC thermograms of dried lead zirconate titanate PZT4 gel from 25°C to 1200°C.

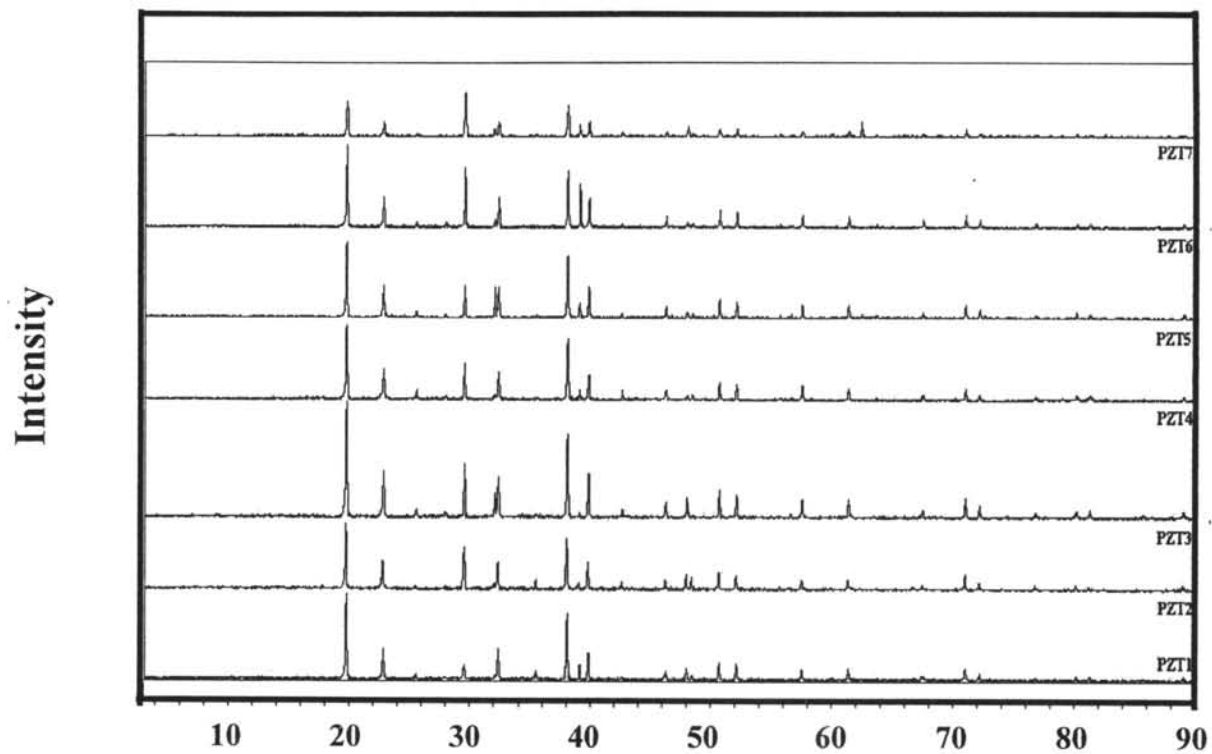


Figure 7.7 XRD diffraction patterns of dried lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ gels: PZT1; PZT2; PZT3; PZT4; PZT5; PZT6; PZT7.

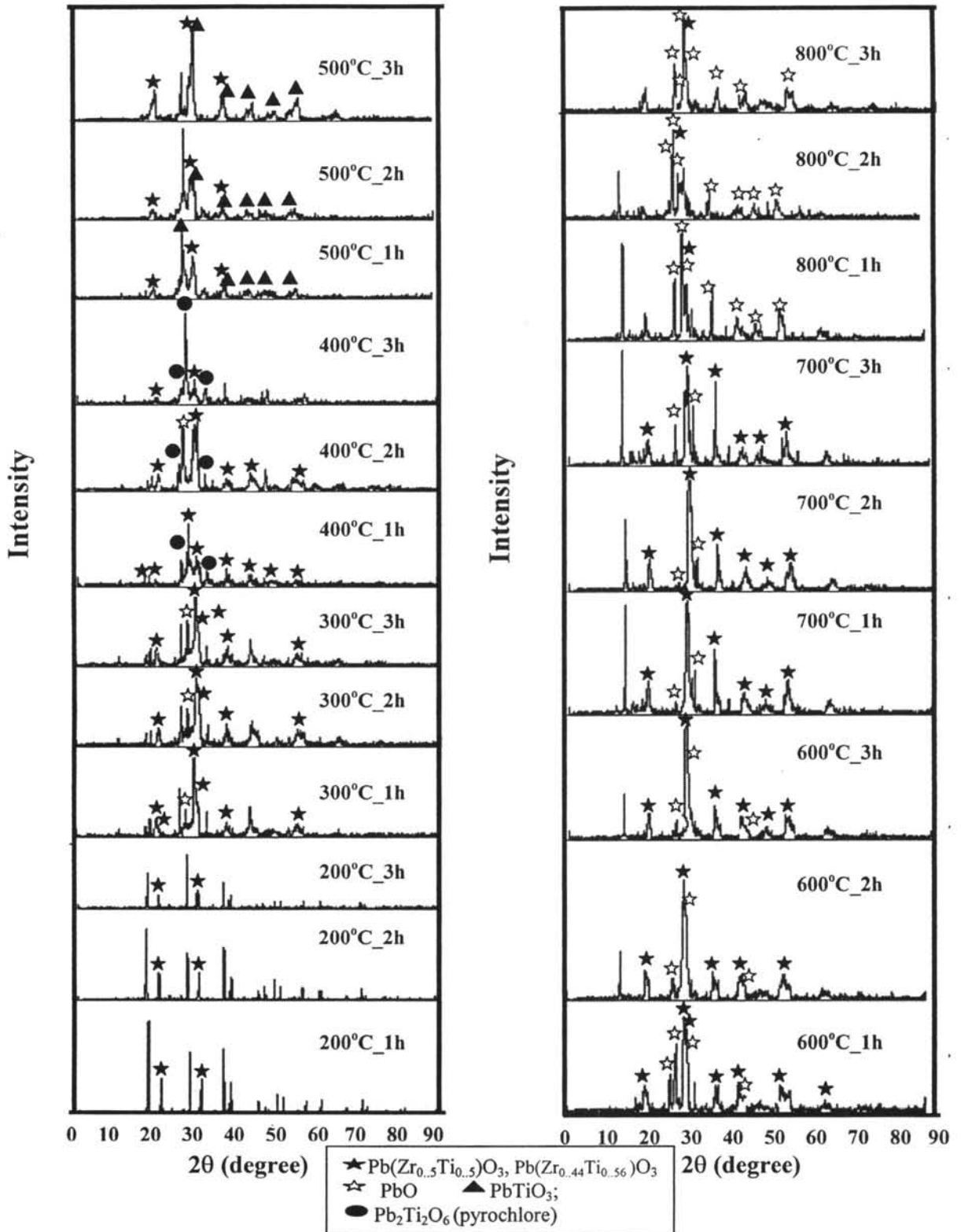


Figure 7.8 XRD diffraction patterns of calcined lead zirconate titanate powders (PZT4) at 200°C; 300°C; 400°C; 500°C; 600°C; 700°C; 800°C for durations of 1, 2, and 3 h.

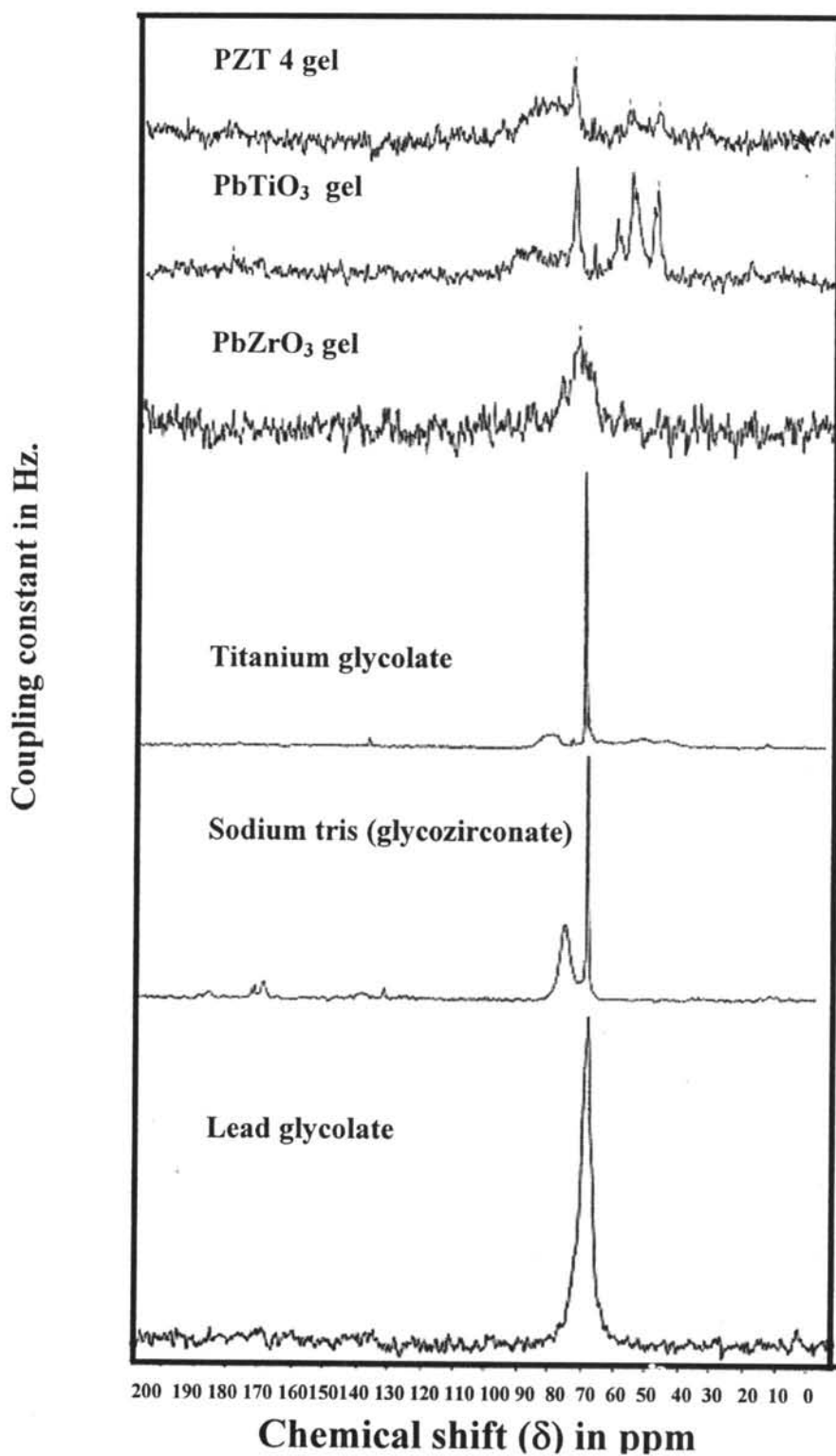


Figure 7.9 ^{13}C -Solid state NMR spectra of the synthesized lead glycolate precursor, sodium tris (glycozirconat) precursor, titanium glycolate precursor, dried PbZrO_3 gel, dried PbTiO_3 gel, and dried PZT4 gel.

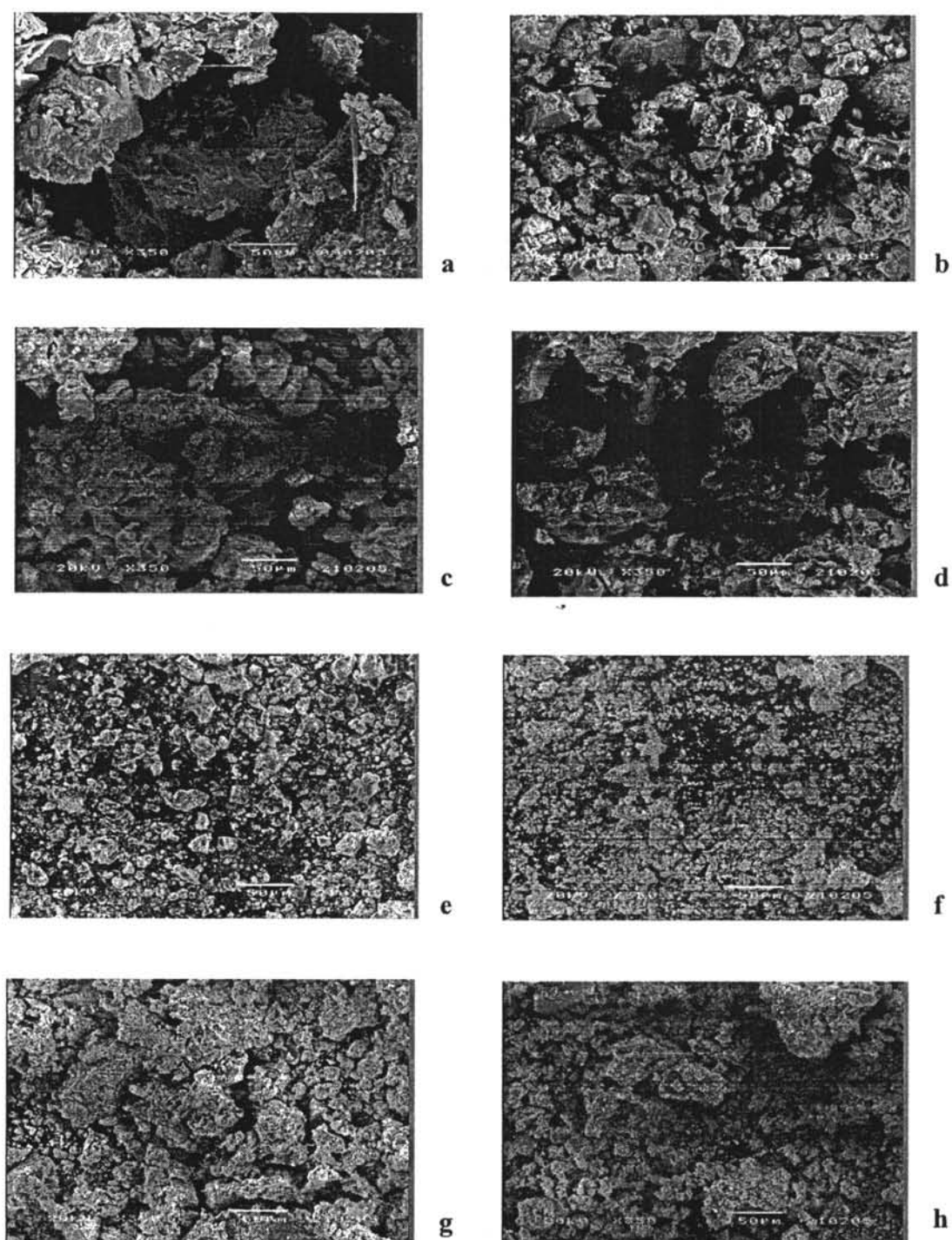


Figure 7.10 SEM micrographs showing microstructure of dried PZT4 gel and calcined PZT4 at: a) 25°; b) 200°C; c) 300°C; d) 400°C; e). 500°C; f) 600°C; g) 700°C; and h) 800°C for 1 h at the magnification of 350.

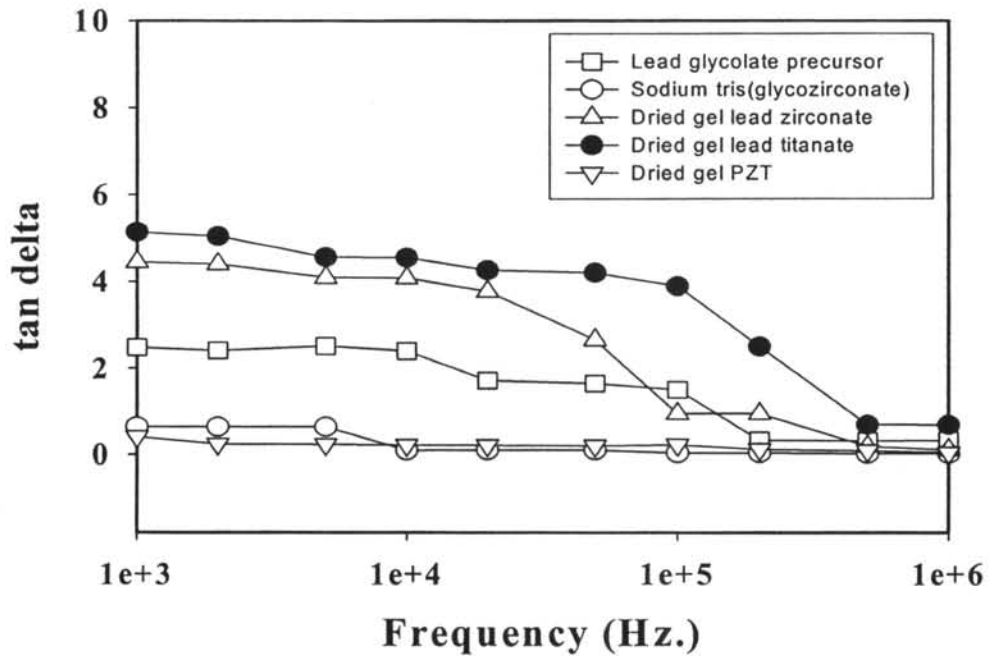
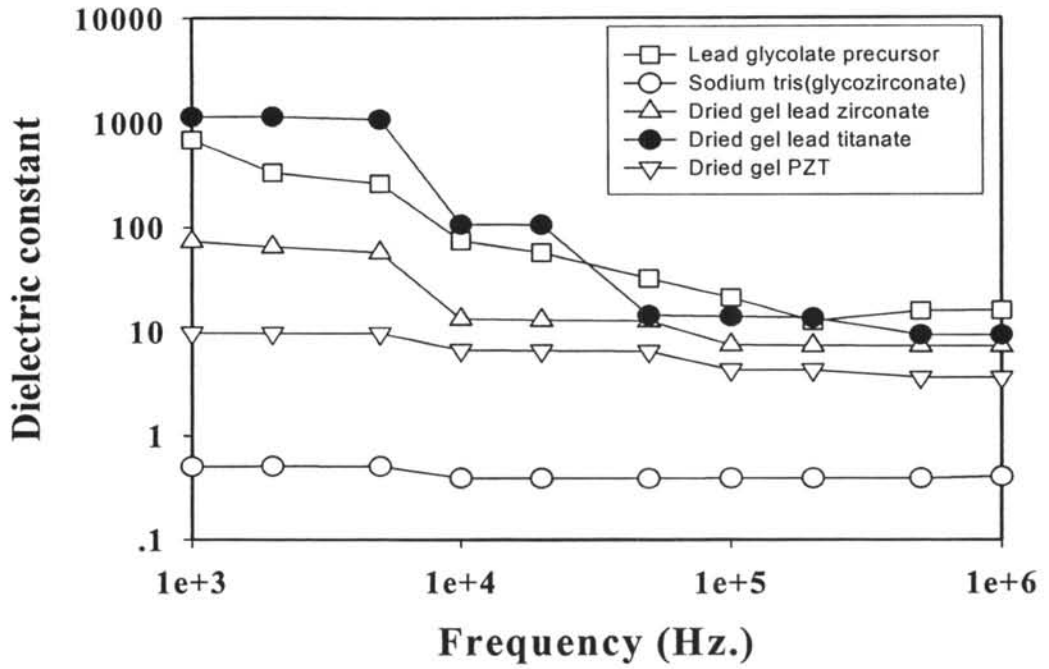


Figure 7.11 Dielectric constant and tan delta of lead glycolate precursor, sodium tris(glycozirconate) precursor, dried lead zirconate gel, dried lead titanate gel, and dried lead zirconate titanate (PZT4) gel vs. frequency measured at room temperature.

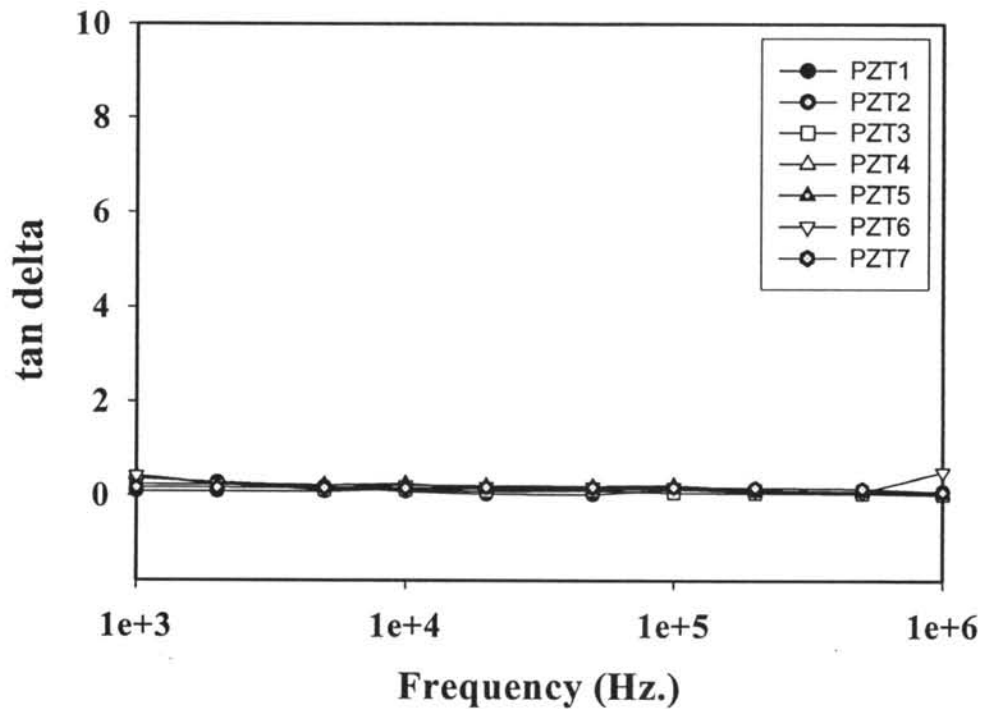
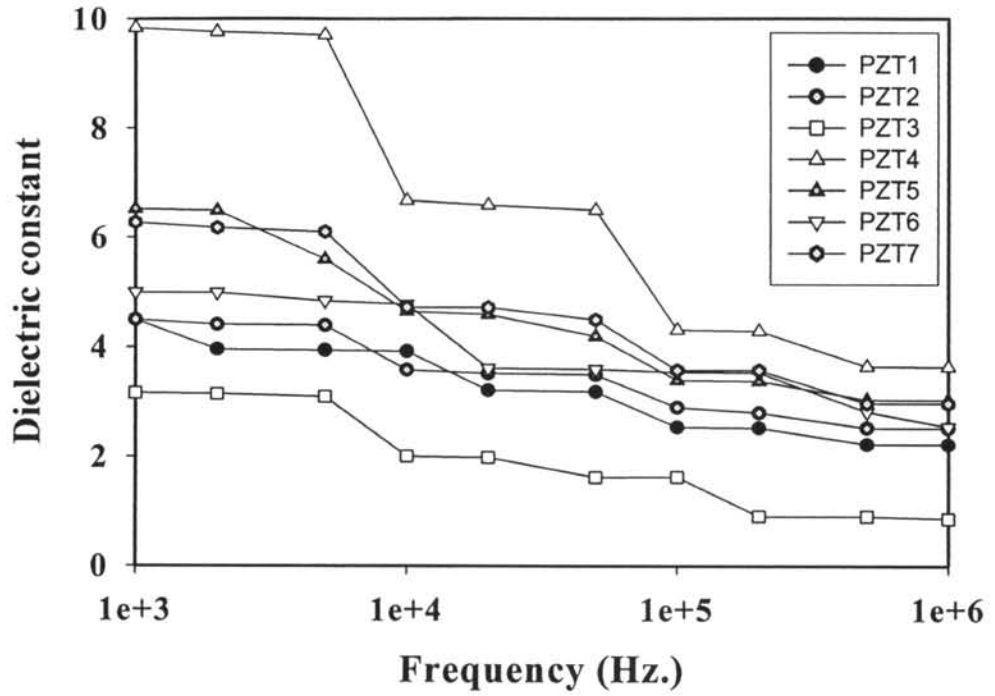


Figure 7.12 Dielectric constant and tan delta of dried lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ gels: PZT1; PZT2; PZT3; PZT4; PZT5; PZT6; PZT7 vs. frequency measured at room temperature.

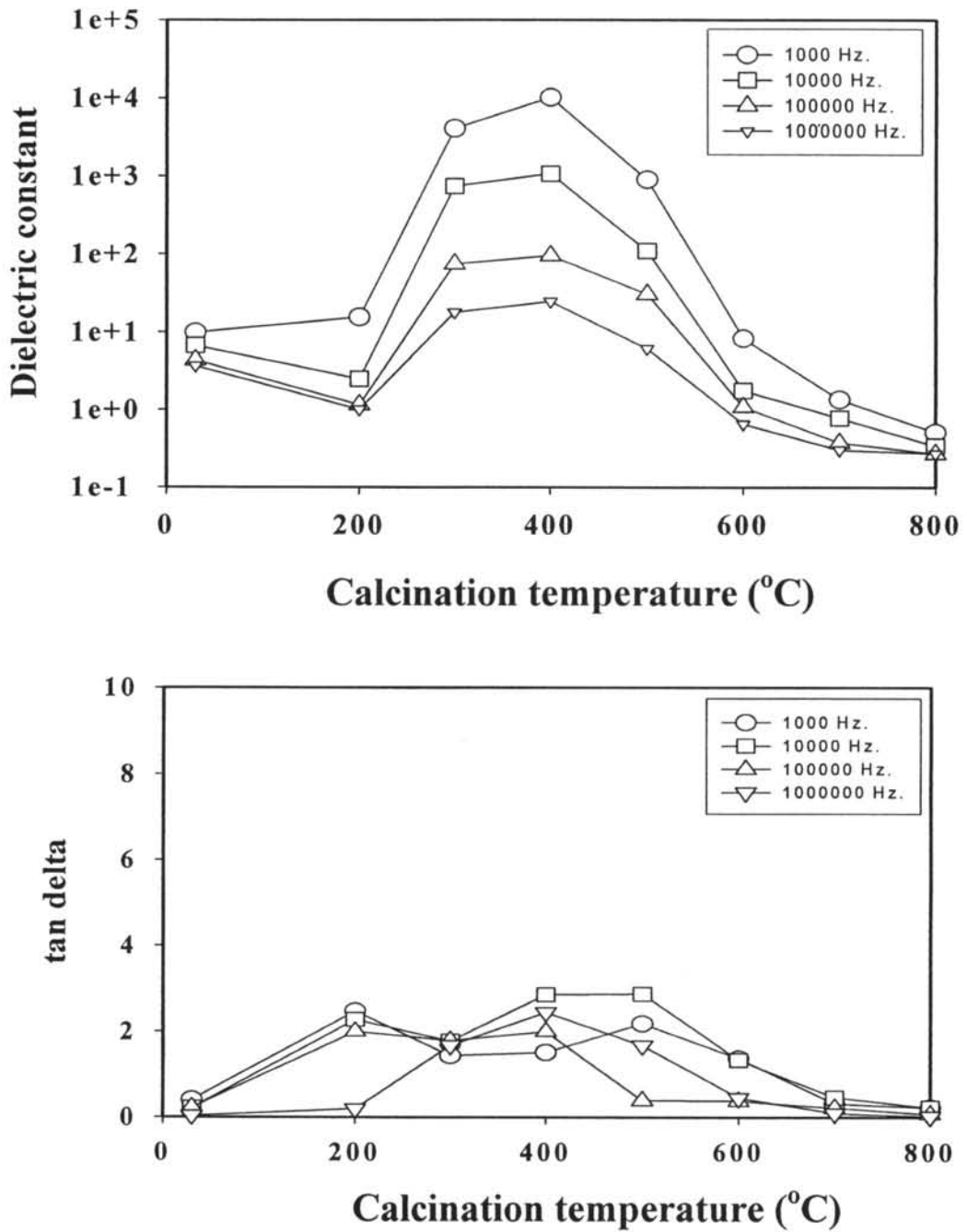


Figure 7.13 Dielectric constant and tan delta of calcined lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT4) vs. calcination temperature (200°C, 300°C, 400°C, 500°C, 600°C, 700°C and 800°C) for 1h at various frequencies.