CHAPTER VI

A NOVEL ROUTE TO PEROVSKITE LEAD ZIRCONATE FROM LEAD GLYCOLATE AND SODIUM TRIS (GLYCOZIRCONATE) VIA SOL-GEL PROCESS

6.1 Abstract

A perovskite lead zirconate was synthesized, using lead glycolate and sodium tris (glycozirconate) as the starting precursors, by the sol-gel process. The obtained molar ratio Pb:Zr of $PbZrO_3$ was 0.9805:1. The TGA-DSC characterizations indicated that the percentage of ceramic yield was 56.4, close to the calculated chemical composition 59.6. The exothermic peak occurred at 245.7°C, close to the theoretical Curie temperature of 230°C. The pyrolysis of $PbZrO_3$ of the perovskite phase was investigated in terms of calcination temperature and time. The structure obtained was the orthorhombic form when calcined at low temperature at 300°C for 1 h; it transformed to the monoclinic and cubic forms of the perovskite phase at higher temperatures above the Curie temperature as verified by X-ray data. The lead zirconate synthesized and calcined at 300°C for 1 h has the highest dielectric constant, the highest electrical conductivity, and the dielectric loss tangent of 2267, 3.058×10^{-4} $(\Omega.m)^{-1}$, and 2.484 at 1000 Hz respectively. The lead zirconate powder produced has potential applications as materials used in microelectronics and microelectro mechanical systems.

Keywords: Lead Zirconate, Lead Glycolate Precursor, Sodium Tris (glycozirconate) Precursor, Anti-ferroelectric and Pyroelectric Materials

6.2 Introduction

Antiferroelectric materials, especially polycrystalline ceramics, are very promising for a variety of devices, such as sensors, actuators, micromotors, microvalves, micropumps, and many other micromechanical devices. Lead zirconate is one kind of antiferroelectric materials having a non-permanent electric dipole moment whose complete or partial realignment can be reversed under appropriate conditions. Lead zirconate can be produced from a variety of processes, such as a conventional co-precipitation or a solid-state reaction of mixed oxides, a sol-gel synthesis, or a hydrothermal reaction [1]. Among these methods, the sol-gel process offers significant advantages: high purity, chemical homogeneity, easily controlled particle size, lower reaction temperature, and better controlling of molecular-level properties. Two major disadvantages of the sol-gel process are the highly expensive and moisture sensitive alkoxide precursors which are used as starting materials [2, 3].

Djuricic *et al.* (1995) studied electrical properties of zirconia samples produced by homogeneous precipitation with using zirconium sulphate tetrahydrate as starting material to react with polyvinyl pyrolidone in water solution calcined at 300°C [4]. Jiye F. *et al.* (1998) synthesized and characterized ultrafine lead zirconate powders via three processes: the conventional solid reaction, the conventional coprecipitation, and the micro emulsion-refined coprecipitation using either oxalic acid or ammonia as the precipitant [5]. Kobayashi *et al.* (1999) studied $PbZrO_3$ at high pressure using x-ray diffraction technique and dielectric spectroscopy to look at its phase transformation. The lead zirconate underwent the phase transformation from the orthorhombic form to the monoclinic form with corresponding dielectric constant of approximately 500 at 1.0 kHz. The Curie temperature was identified at 230°C in the cubic form [6]. Pradhan *et al.* (2001) synthesized a stoichiometric lead zirconate at low temperature by coprecipitation in non-aqueous medium. The lead acetate and zirconium oxychloride were used as starting materials in NaOH – ethylene glycol solution at 60°C, 24 h. and calcined at 600°C [7]. Furuta *et al.* (1999) investigated the phase transition of the polycrystalline fine-powder $PbZrO_3$ under high pressure using Raman scattering technique [8]. Tang and Tang (2003) investigated lead zirconate thin films by mixing lead acetate trihydrate Pb

$(CH_3COO)_2.3H_2O$ with zirconium n-propoxide $Zr(O(CH_2)_2CH_3)_4$ in 2-methoxyethanol solution [9].

From these previous studies, the sol-gel process emerges as a possible method to produce lead zirconate from lead and zirconium (IV) alkoxide precursors, although these precursors are usually moisture sensitive. Wongkasemjit *et al.* [10-13] 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 was to synthesize high purity lead zirconate ($PbZrO_3$) via the sol-gel process using lead glycolate [12] and sodium tris (glycozirconate) [10] as the moisture stable precursors. We also investigated the influence of the calcination temperature and time on morphology, electrical properties, and phase transformation.

6.3 Experimental

Materials

The starting raw material, lead glycolate and sodium tris (glycozirconate) were synthesized by the oxide one pot synthesis process (OOPS) [10-13] which were less moisture sensitive.

UHP grade nitrogen; 99.99% purity was obtained from Thai Industrial Gases Public Company Limited (TIG). Lead acetate trihydrate $Pb(CH_3COO)_2.3H_2O$ containing 99.5% purity was purchased from Asia Pacific Specialty Chemical Limited (Australia). Zirconium (IV) hydroxide $Zr(OH)_4$ 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 (Polymer TOF-Brucker) using sinapinic acid as a matrix, cesium gun as indicator, and cesium iodide (CsI) as a standard for peak calibration. An elemental analyzer was used to characterize CHNS/O compositions (Perkin Elmer, PE 2400 Series II) through pyrolysis. Fourier transform infrared spectra (FTIR) were recorded on a VECTOR 3.0 BRUKER spectrometer with a spectral resolution of 4 cm^{-1}. A thermal gravimetric analysis (TGA) and a differential thermal analysis (DTA) were carried out using a Perkin Elmer thermal analysis system with a heating rate of 10°C/min over a 25°-800°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 a Philips Electronics analyzer (N.V. 1999) consisting CuKα radiation (λ = 0.154nm). Micrographs were obtained using a scanning electron microscope (SEM, 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 (XGT 2000w, Horiba, Japan).

Starting Material Preparation

Lead Glycolate

Lead glycolate was synthesized via the OOPS process [12]. A mixture of lead acetate trihydrate ($Pb(CH_3COO)_2.3H_2O$, 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) acting as a catalyst was heated at the boiling point of EG under N_2 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 was changed to be yellow or golden brown. The reaction mixture was cooled to obtain 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} (νC-H), 1086, 1042 cm^{-1} (νC-O-Pb bond), and 573 cm^{-1} (νPb-O bond) were observed as shown in Fig. 6.1. ^{13}C-solid state NMR:

only one single peak at 68.6 ppm appeared due to $\underline{C}H_2$-OH of EG. From the EA analysis, we found 8.864% in C and 1.392% in H which can be compared with the calculated values of 8.990% in C and 1.498% in H. From the FAB^+-MS analysis, we obtained approximately 55% of the highest m/e at 801 for $[-(-PbOCH_2CH_2O-)_3-]$, 25% intensity at 595 for $[-OCH_2CH_2OPbOCH_2CH_2OPbOCH_2CH_2O-+H^+]$ and 56% intensity at m/e 505 for $[-CH_2OPbOCH_2CH_2OPb-+H^+]$. From the DSC-TGA analysis, a decomposition transition occurred at 290°-305°C, with a 82.5% ceramic yield $(-PbOCH_2CH_2O-)_3$.

<u>Sodium Tris(glycozirconate)</u>

Sodium tris (glycozirconate) was also synthesized via the OOPS process [11]. 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 of 2939-2873 cm^{-1} (νC-H) and 1090 cm^{-1} (νC-O-Zr bond) were observed as shown in Fig. 6.1. 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} belonging 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 [11]. The thermal behavior was investigated by means of TGA and DSC measurements. The TGA-DSC profiles of sodium tris (glycozirconate) complex have one major thermal decomposition ranging from 350° to 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 of the product framework. The experimental weight loss is consistent with the theoretical weight loss calculated for the formation of the proposed product $Na_2O.ZrO_2$, which turned out to be 41.67%. The percentage ceramic yield of the product was 58.41%, in excellent agreement with the theoretical value (58.33%). In addition, EDS was used to confirm the formation of $Na_2O.ZrO_2$ after thermal decomposition. The resulting Na/Zr ratio was equal to 1.98, which is 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 CH_2-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 (glycozircanate) precursor, the analytically calculated values are (%): C, 22.70; H, 3.78. We obtained experimental values of (%):C, 22.41; H, 4.23. The MS spectrum fragmentation patterns can be employed on the basis of proposed structure at m/e 635 (11.5 % intensity), 297 (87.6%), 182 (100%), and 151 (80.7%).

Sol-gel Preparation of Lead Zirconate

The sol-complex alkoxide mixture was prepared by mixing 2 x 10^{-2} g of lead glycolate (Pb content equal to 1.6 x 10^{-2}g) in a 0.1 M nitric solution (HNO_3) with 1.3 x 10^{-2} g of sodium tris (glycozirconate) (Zr content equal to 3.6 x 10^{-3} g) dissolved in water. The two solutions were then mixed together, and a white turbid solution was obtained. The sol to gel transition occurred within a few seconds, and a small amount of water was required to adjust pH to be in the range of 8-9 at room temperature. The gels were allowed to settle at room temperature and kept at 50°C for 2 days, and finally we obtained a light yellow gel. The gels were calcined at 200°, 300°, 400°, 500°, 600° and 700°C for 1, 2 and 3 h and characterized.

Electrical Properties Characterization

The samples were prepared according to the ASTM B263-94 standard for electrical properties. 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 were measured at frequency between 10^3-10^6 Hz [16, 17].

6.4 Results and Discussion

Lead Zirconate Gel and Calcined Lead Zirconatesl Characterization

FTIR sprectrum of dried lead zirconate gel is shown in Fig. 6.1 for comparison with FTIR spectra of lead glycolate precursor and sodium tris(glycozirconate) precursor. Figure 6.2 shows FTIR spectra of dried lead zirconate gels of various mole ratios between lead glycolate and sodium tris (glycozirconate) precursors (1:1; 1:2; 1:3; 1:4; 2:1; 3:1; and 4:1). There appear a visible broad peak of at 3500 cm^{-1} (νO-H) [2], smaller peaks at 1660, 1487, and 1100 cm^{-1} (νC-O-Zr) [12-13], and a peak at 796 cm^{-1} (νC-O-Pb) [18]. The broad peak at 771 cm^{-1} also can be identified as the Pb-O-Zr stretching [2, 12-13, 18]. The peak at 2300 cm^{-1} can be identified as the stretching of CO_2 [18].

A thermogram of dried lead zirconate gel, obtained from the TGA-DTA technique, at temperature between 25°C and 1000°C is shown in Fig. 6.3. The weight loss of dried lead zirconate gel was 43.6%; the percentage of ceramic yield obtained was then 56.4%, close to theoretically calculated-chemical composition 59.6. The maximum value of weight loss occurred at 250°- 300°C by exothermic reactions. Our result is consistent with the results obtained by Yu *et al.* and Kumar *et al.* [2, 14]. The sharp exothermic peak at 245.7°C resulted from the heat of vaporization of EG generated from the hydrolysis. The exothermic broad peak occurred close to the lead titanate Curie temperature of 230°C, indicating the phase transformation from the orthorhombic form (antiferroelectric) to the cubic form (paraelectric) of $PbZrO_3$ in the perovskite phase [6,8]. In addition, there was also the exothermic reaction of PbO-$PbZrO_3$ eutectic liquid existing at 716.8°C.

Raman spectra of lead glycolate precursor, sodium tris (glycozirconate) precursor, and dried lead zirconate gel are shown in Fig.6.4 where the spectrum of the latter shows a broad band indicating its amorphous structure. Figure 6.5 shows Raman spectra of dried lead zirconate gels of mole ratio 1:1 at room temperature and at calcination temperatures of 200°, 300°, 400°, 500°, 600°, and 700°C, and at 1 hr. For calcination temperatures between 200°C to 400°C, there are two distinct peaks at 450 cm^{-1} and 700 cm^{-1} indicating that the gels became more crystalline with increasing calcination temperature. For calcination temperatures between 500°C and 700°C, there appear two peaks in the Raman spectra at 550 cm^{-1} and 660 cm^{-1} displaying crystallinity of other structures.

The microstructure transformation of our calcined samples can be observed from SEM micrographs as shown in Fig.6.6. Lead zirconate particles became agglomerated starting at 200°C, as shown in Figure 6.6b. For calcination temperatures above 300°C, the phase transformation can be observed from the orthorhombic structure (Fig. 6.6c, 300°C) to the mixed orthorhombic and monoclinic structures (Figs. 6.6d, 6.6e, 400 and 500°C). The cubic form of the perovskite phase can be observed in Fig. 6g at the calcination temperature of 700°C [18, 19].

XRD peak patterns of lead zirconate samples calcined at 200°, 300°, 400°, 500°, 600° and 700°C and at various calcination times of 1, 2 and 3 h are shown in Fig.6.7. For calcination temperature of 200°C, we obtained the mixed orthorhombic structures ($PbZrO_3$ [orthorhombic] + Pb-O-lead glcolate + t-ZrO_2). For calcination temperature of 300°C at 1 h, we obtained only the pure orthorhombic structure ($PbZrO_3$ [orthorhombic]). For calcination temperature between 300°C at 2 h and 400°C at 3 h, we obtained a mixture of the orthorhombic and the monoclinic structures ($PbZrO_3$ [orthorhombic] + $PbZrO_3$ [monoclinic]). For calcination temperature between 500°C at 1 h and 600°C at 3 h, we obtained a mixture of the orthorhombic, the monoclinic and the cubic structures ($PbZrO_3$ [orthorhombic] + $PbZrO_3$ [monoclinic] + $PbZrO_3$ [cubic]) [15]. Finally, at calcination temperature of 700°C between 1 to 3 h, we obtained only the cubic structure ($PbZrO_3$ [cubic]). These peaks in Fig. 6.7 can be compared with those of the Joint Committee on Powder Diffraction Standards(JCPDS) patterns of (20-608), and (35-739) [1-2, 7-8].

The percentage chemical compositions of calcined samples were analyzed by an X-ray analytical microscope and data are tabulated as shown in Table 6.1. The experimental mole ratio of PbO / ZrO_2 is close to the theoretically calculated mole ratio of the lead zirconate, which is 0.9805:1.00. From the elemental analysis, data were used to calculate the percentage of carbon which turns out to be 5.106 ± 0.114, a value close to theoretically calculated chemical composition 5.381. From the mass spectroscopy, we obtained a molecular weight of 892 g/mol for our calcined samples. Based on these data, we proposed the structure shown in Table 6.2.

Electrical Properties of Synthesized Lead Zirconate

Figures 6.8a and 6.8b show the dielectric constants and dielectric loss tangents of the starting precursors and dried lead zirconate gel as function of frequency at 27°C. It can be seen that the lead glycolate possesses the highest dielectric constant at 1000 Hz and the highest electric conductivity; namely, 691 and 8.85×10^{-5} S/m, respectively. The dielectric constants and the dielectric loss tangents of the three materials generally decrease with increasing frequency, indicative of the polarization mechanisms involved: the electronic, atomic, dipole, and interfacial polarizations [20].

Table 6.3 lists dielectric constants and dielectric loss tangents, at 1000 Hz and at 27°C, and electrical conductivity of the two precursors, dried lead zirconate gel, and our calcined lead zirconate samples of various calcination temperatures and times. Among these samples, it can be seen that $PbZrO_3$ 300_1h, lead zirconate calcined at 300°C for a duration of 1h, possesses the highest dielectric constant of 2267, with corresponding dielectric loss tangent of 2.484, and the highest DC electrical conductivity of 3.058×10^{-4} S/m. This calcined sample corresponds to the pure orthorhombic structure of the perovskite phase, as shown previously from the X-ray data of Fig. 6.7. For the orthorhombic form of the perovskite phase, we may expect antiferroeletric property [18]. At higher calcination temperatures, above the Curie temperature of 247°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, as accompanied by paraelectricity [18].

Figures 6.9a and 6.9b show the dielectric constants and the dielectric loss tangents of lead zirconates of various frequencies as functions of calcination temperature. $PbZrO_3$ 300_1h possesses the highest dielectric constant at all frequencies investigated: 1000, 10,000, 100,000, and 1,000,000 Hz. On the other hand, the dried lead zirconate gel possesses the highest dielectric loss values in the same frequency range.

6.5 Conclusions

The synthesis of lead zirconate by the sol-gel process using lead glycolate and sodium tris (glycozirconate) as starting precursors gave high purity and low moisture sensitivity light yellow color powder. The experimental stoichiometry value between PbO and ZrO_2 is 0.9805:1.00, close to theoretically calculated theoretical value of $PbZrO_3$. The lead zirconate gel was dried and calcined below T_c (245.7°C) in order to prevent the structural change from the orthorhombic form to the cubic form of the perovskite phase. The highest dielectric constant of 2267 conductivity of 3.058×10^{-4} $(\Omega.m)^{-1}$, and low dielectric loss tangent of 2.484 measured at 1000 Hz.

were obtained from the $PbZrO_3$ calcined at 300°C for 1 h. Dielectric constant and conductivity decreased with calcination time and temperature when it was above the T_c. Our synthesized materials appear to be a suitable candidate for using as an electronic-grade $PbZrO_3$.

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6.7 References

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Captions of Figures and Tables

Figure 6.1	FTIR spectra of lead glycolate precursor, sodium tris (glycozirconate) precursor, and lead zirconate gel at the mole ratio 1:1.
Figure 6.2	FTIR spectra of the lead zirconate gels at the mole ratio 1:1; 1:2; 1:3; 1:4; 2:1; 3:1; and 4:1.
Figure 6.3	The TGA-DSC thermograms of dried lead zirconate gel from 25°C to 1000°C.
Figure 6.4	Raman spectra of lead glycolate precursor, sodium tris (glycozirconate) precursor, and dried lead zirconate gel.
Figure 6.5	Raman spectra of dried lead zirconate gel, calcined lead zirconates at 200°; 300°; 400°; 500°; 600°; 700°C for 1h. from 200-1000 cm^{-1}.
Figure 6.6	SEM micrographs showing the phase transformation of dried lead zirconate gel and calcined lead zirconates at: a) 25°; b) 200°; c). 300°; d) 400°; e). 500°; f) 600°; and g) 700°C for 1 (column1), 2 (column2), and 3 (column3) h at the same magnification of 1,500.
Figure 6.7	XRD diffraction patterns of dried lead zirconate gel, and calcined lead zirconates at calcination temperatures of 200°; 300°; 400°; 500°; 600°; 700°C for durations of 1, 2, and 3h.
Figure 6.8	Dielectric constant and tan delta of lead glycolate precursor, sodium tris(glycozirconate), and dried lead zirconate gel vs. frequency measured at room temperature.
Figure 6.9	Dielectric constant and tan delta of calcined temperature lead zirconates at 200°, 300°, 400°, 500°, 600°, and 700°C for 1h. at various frequencies.

Table 6.1 The percentages of chemical compositions of dried lead zirconate gel and calcined lead zirconate samples with the Pb:Zr mole ratio.

Table 6.2 The proposed structure and the percentage of carbon content of lead zirconate.

Table 6.3 The dielectric properties (1000 Hz., 27°C) and DC electrical conductivity of lead glycolate, sodium tris(glycozirconate), dried lead zirconate gel, and calcined lead zirconate samples.

Table 6.1 The percentages of chemical compositions of dried lead zirconate gel and calcined lead zirconate samples with the Pb:Zr mole ratio.

Samples	%Pb	%Zr	%O	%PbO	%ZrO_2	Molar ratio Pb:Zr
Dried $PbZrO_3$ gel	59.23	26.80	13.98	63.80	36.21	0.9721
$PbZrO_3$ 200_1h	59.41	26.66	13.94	63.99	36.01	0.9802
$PbZrO_3$ 200_2h	58.58	27.32	14.11	63.10	36.90	0.9433
$PbZrO_3$ 200_3h	59.86	26.30	13.85	64.48	35.52	1.0001
$PbZrO_3$ 300_1h	57.69	28.03	14.29	64.00	36.00	0.9805
$PbZrO_3$ 300_2h	60.75	25.59	13.67	65.44	34.56	1.0445
$PbZrO_3$ 300_3h	59.57	26.52	13.91	64.18	35.82	0.9883
$PbZrO_3$ 400_1h	61.68	24.84	13.48	66.45	33.55	1.0923
$PbZrO_3$ 400_2h	57.16	28.44	14.39	61.58	38.42	0.8838
$PbZrO_3$ 400_3h	60.87	25.49	13.64	65.57	34.43	1.0505
$PbZrO_3$ 500_1h	59.39	26.67	13.94	63.98	36.02	0.9798
$PbZrO_3$ 500_2h	61.37	25.09	13.54	66.11	33.89	1.0762
$PbZrO_3$ 500_3h	59.73	26.40	13.87	64.35	35.65	0.9955
$PbZrO_3$ 600_1h	57.96	27.81	14.23	62.43	37.57	0.9168
$PbZrO_3$ 600_2h	58.48	27.39	14.13	63.00	37.00	0.9392
$PbZrO_3$ 600_3h	58.22	27.60	14.18	62.72	37.28	0.9284
$PbZrO_3$ 700_1h	57.37	28.28	14.35	61.80	38.20	0.8921
$PbZrO_3$ 700_2h	57.21	28.41	14.38	61.63	38.37	0.8859
$PbZrO_3$ 700_3h	59.77	26.36	13.86	64.39	35.61	0.9972

Table 6.2 The proposed structure and the percentage of carbon content of lead zirconate.

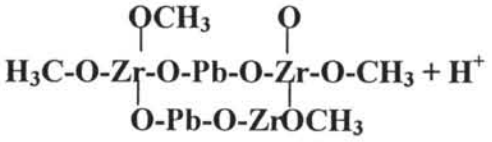
M/e	**Proposed structure**	**% carbon con tent (experimen tal)**	**% carbon content (calculated chemi cal composition)**
892	 $H_3C\text{-}O\text{-}\overset{OCH_3}{Zr}\text{-}O\text{-}Pb\text{-}O\text{-}\overset{O}{Zr}\text{-}O\text{-}CH_3 + H^+$ $O\text{-}Pb\text{-}O\text{-}ZrOCH_3$	**5.106 ± 0.114**	**5.381**

Table 6.3 The dielectric properties (1000 Hz., 27°C) and DC electrical conductivity of lead glycolate, Sodium tris (glycozirconate), dried lead zirconate gel, and calcined lead zirconate samples.

Samples	Dielectric constant	Dielectric loss tangent (tan δ)	Conductivity $(\Omega.m)^{-1}$
Sodium tris(glycozirconate) precursor	0.5077	0.635	1.781×10^{-8}
Lead glycolate precursor	691.70	2.481	8.850×10^{-5}
Dried lead zirconate gel	73.76	4.448	1.516×10^{-5}
$PbZrO_3$ 200_1h	3.514	0.254	1.944×10^{-8}
$PbZrO_3$ 200_2h	451.6	2.719	6.640×10^{-5}
$PbZrO_3$ 200_3h	921.6	3.746	1.876×10^{-4}
$PbZrO_3$ 300_1h	2267	2.484	3.058×10^{-4}
$PbZrO_3$ 300_2h	456.2	4.459	1.175×10^{-4}
$PbZrO_3$ 300_3h	28.67	2.353	3.589×10^{-6}
$PbZrO_3$ 400_1h	25.14	3.291	4.884×10^{-6}
$PbZrO_3$ 400_2h	3.798	0.265	5.834×10^{-8}
$PbZrO_3$ 400_3h	2.210	0.017	2.227×10^{-9}
$PbZrO_3$ 500_1h	2.553	0.131	1.895×10^{-8}
$PbZrO_3$ 500_2h	1.873	0.062	6.509×10^{-9}
$PbZrO_3$ 500_3h	2.663	0.310	4.677×10^{-8}
$PbZrO_3$ 600_1h	2.741	0.212	3.183×10^{-8}
$PbZrO_3$ 600_2h	0.867	0.532	2.451×10^{-8}
$PbZrO_3$ 600_3h	1.651	0.077	7.186×10^{-9}
$PbZrO_3$ 700_1h	2.469	0.021	1.859×10^{-9}
$PbZrO_3$ 700_2h	2.556	0.006	9.804×10^{-10}
$PbZrO_3$ 700_3h	2.500	3.436	1.190×10^{-10}

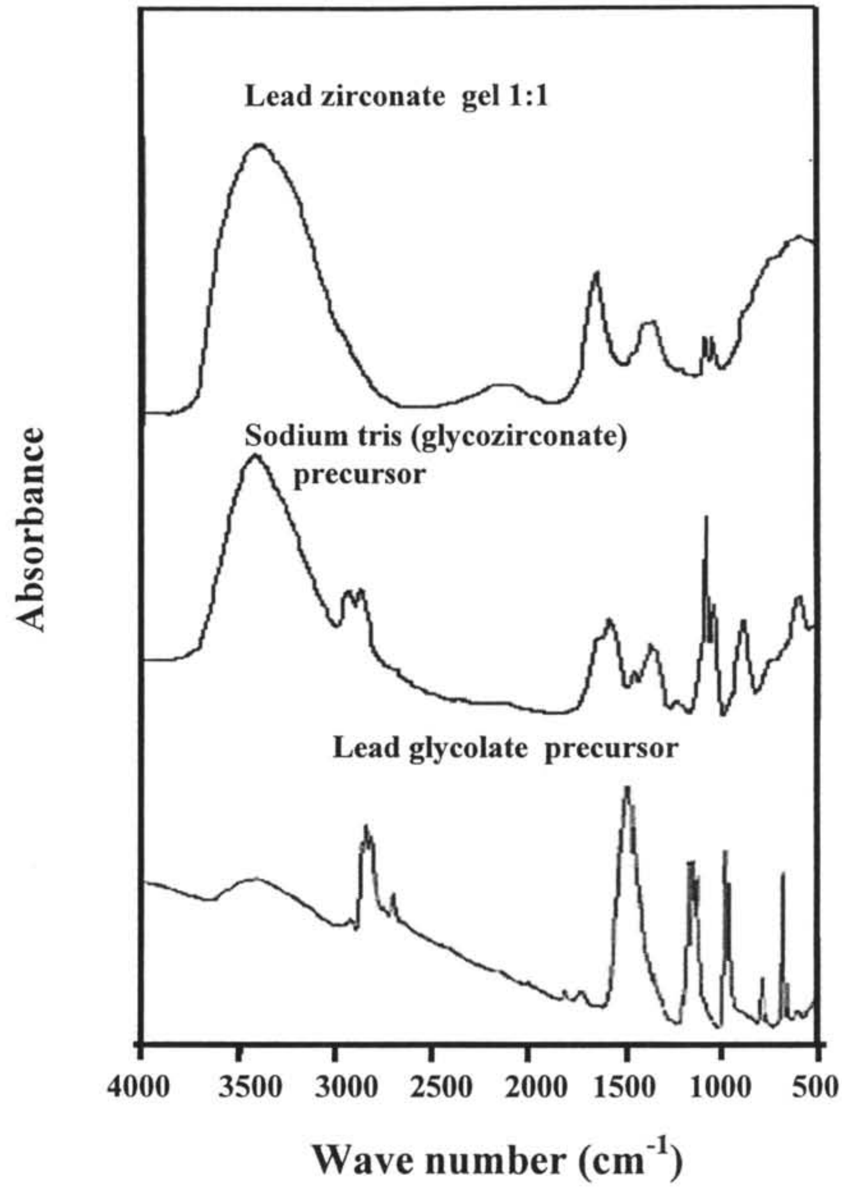


Figure 6.1 FTIR spectra of lead glycolate precursor, sodium tris (glycozirconate) precursor, and lead zirconate gel at the mole ratio 1:1.

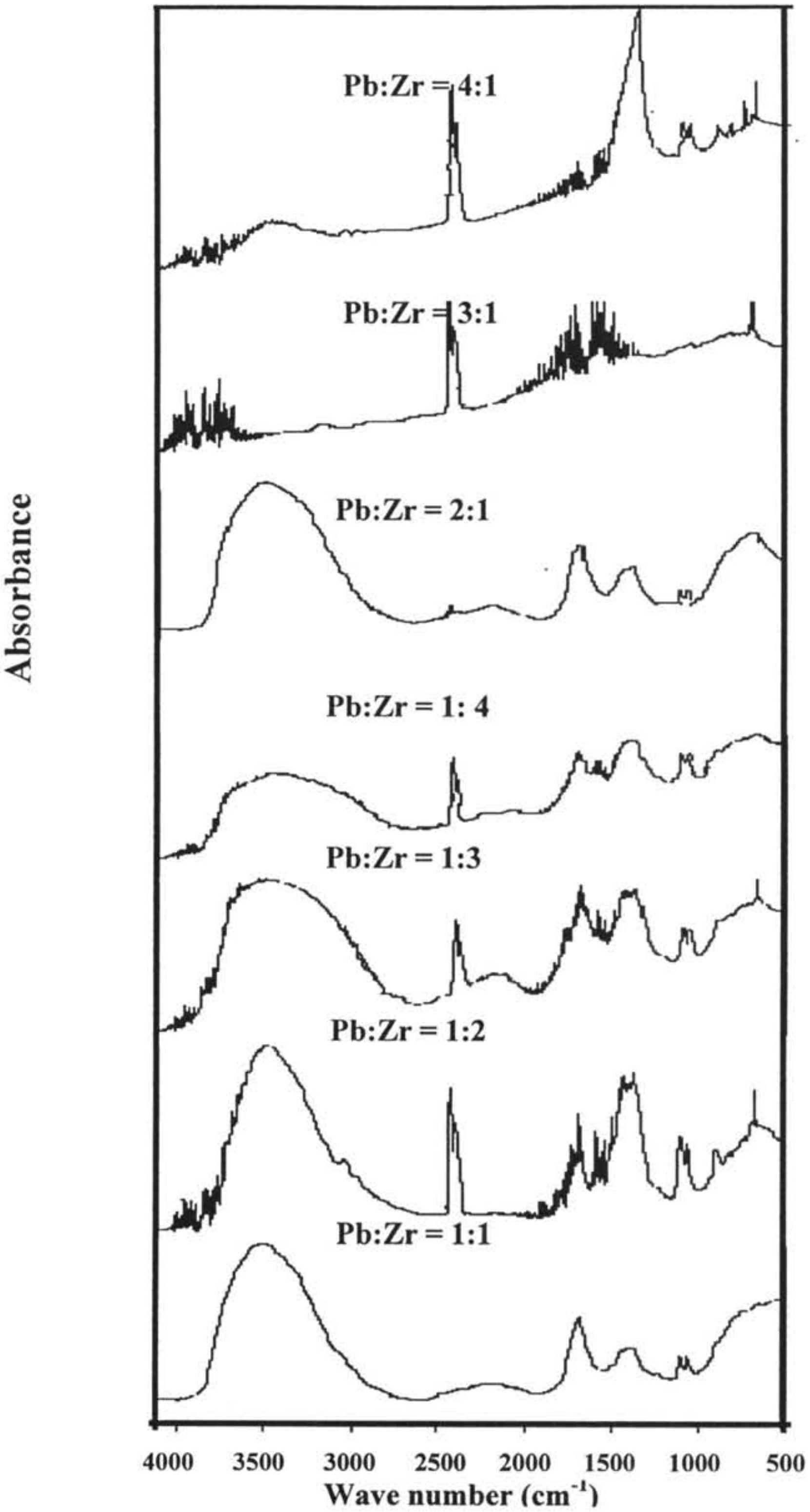


Figure 6.2 FTIR spectra of the lead zirconate gels at the mole ratio 1:1; 1:2; 1:3; 1:4; 2:1; 3:1; and 4:1.

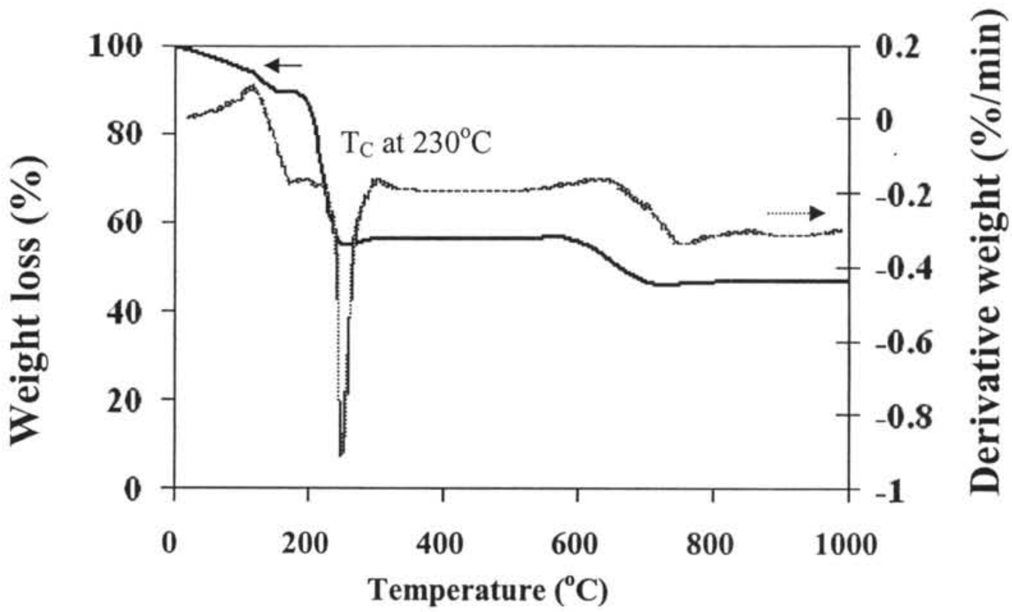


Figure 6.3 The TGA-DSC thermograms of dried lead zirconate gel from 25°C to 1000°C.

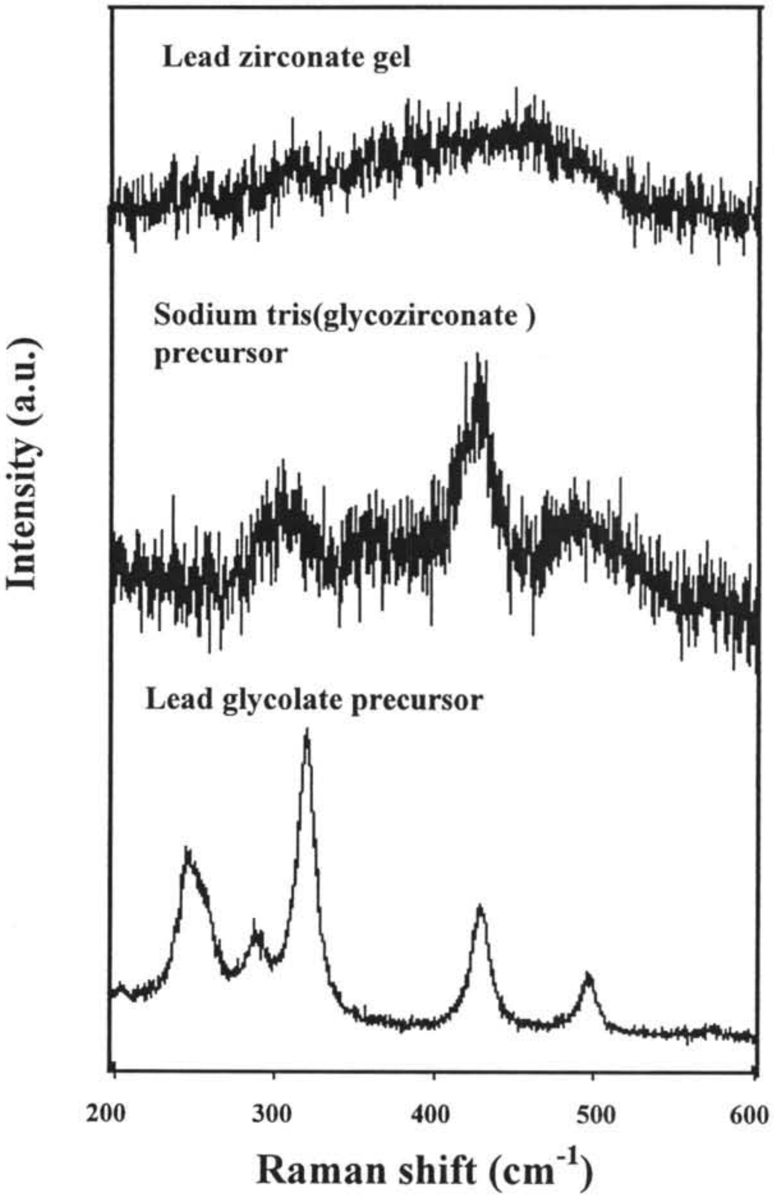


Figure 6.4 Raman spectra of lead glycolate precursor, sodium tris (glycozirconate) precursor, and dried lead zirconate gel.

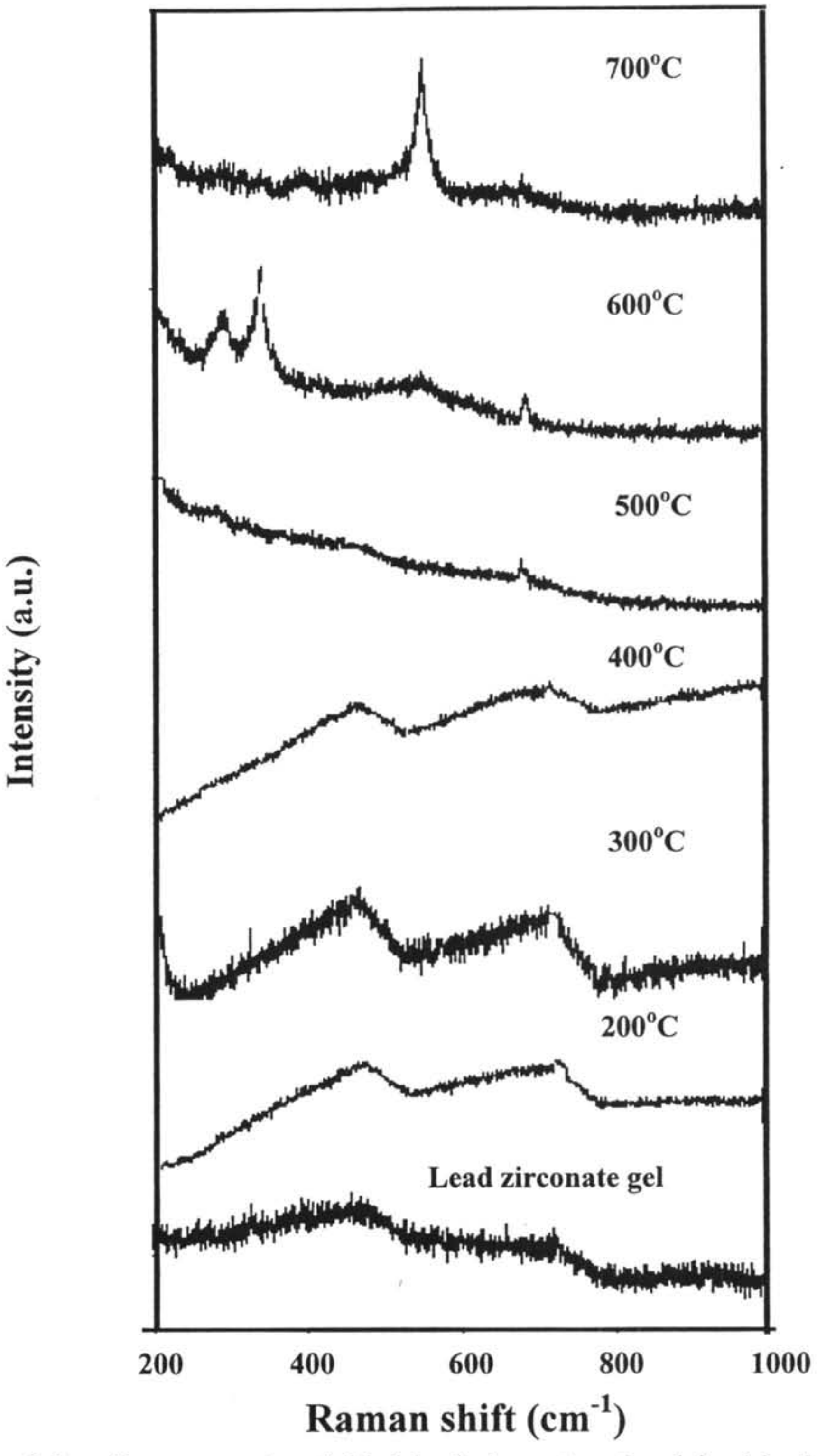
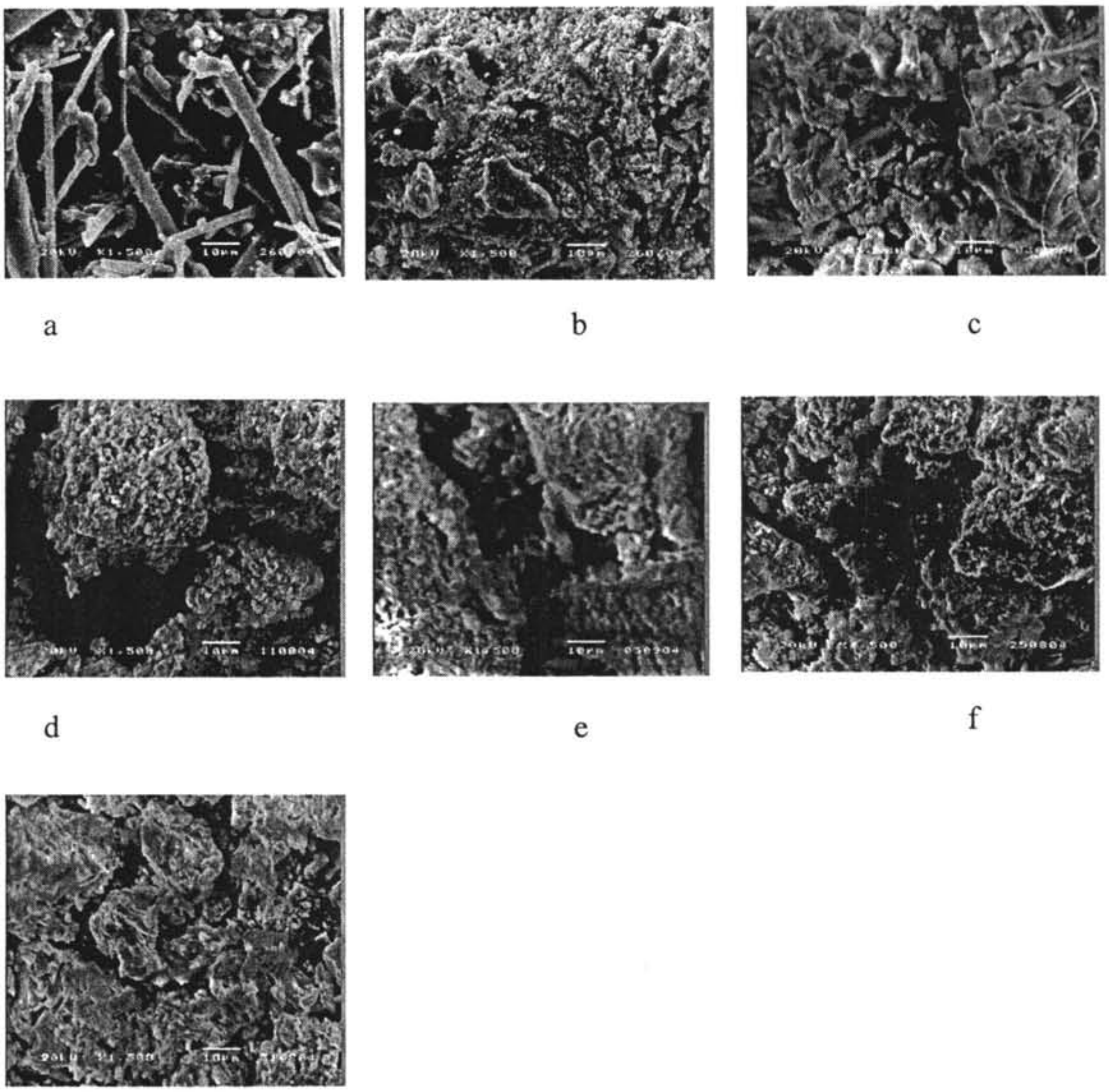


Figure 6.5 Raman spectra of dried lead zirconate gel, calcined lead zirconates at 200°; 300°; 400°; 500°; 600°; 700°C for 1h. from 200-1000 cm^{-1}.



a b c

d e f

g

Figure 6.6 SEM micrographs showing the phase transformation of dried lead zirconate gel and calcined lead zirconates at: a) 25°; b) 200°; c). 300°; d) 400°; e). 500°; f) 600°; and g) 700°C for 1 (column1), 2 (column2), and 3 (column3) h at the same magnification of 1,500.

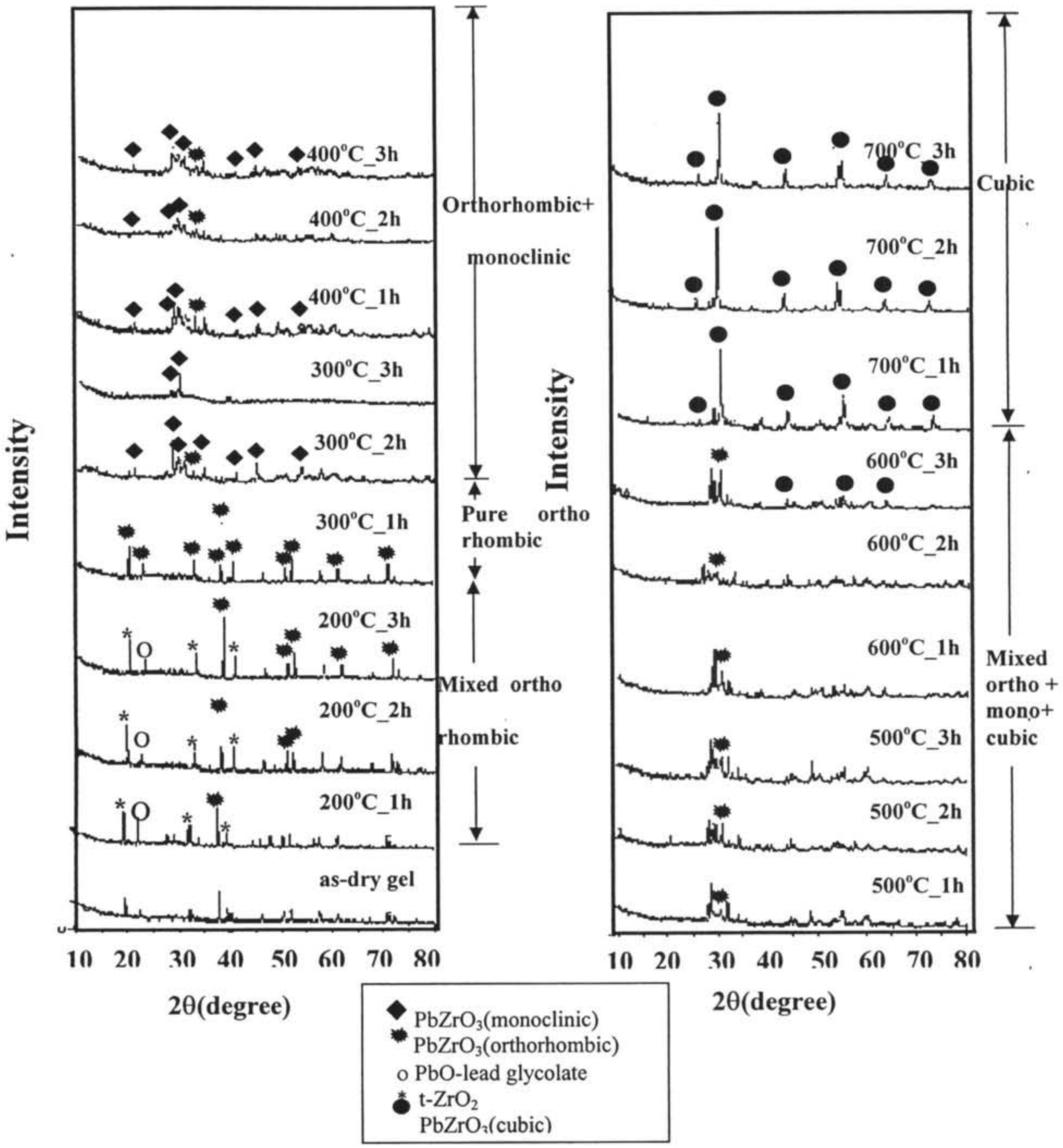


Figure 6.7 XRD diffraction patterns of dried lead zirconate gel, and calcined lead zirconates at calcination temperatures of 200°; 300°; 400°; 500°; 600°; 700°C for durations of 1, 2, and 3h.

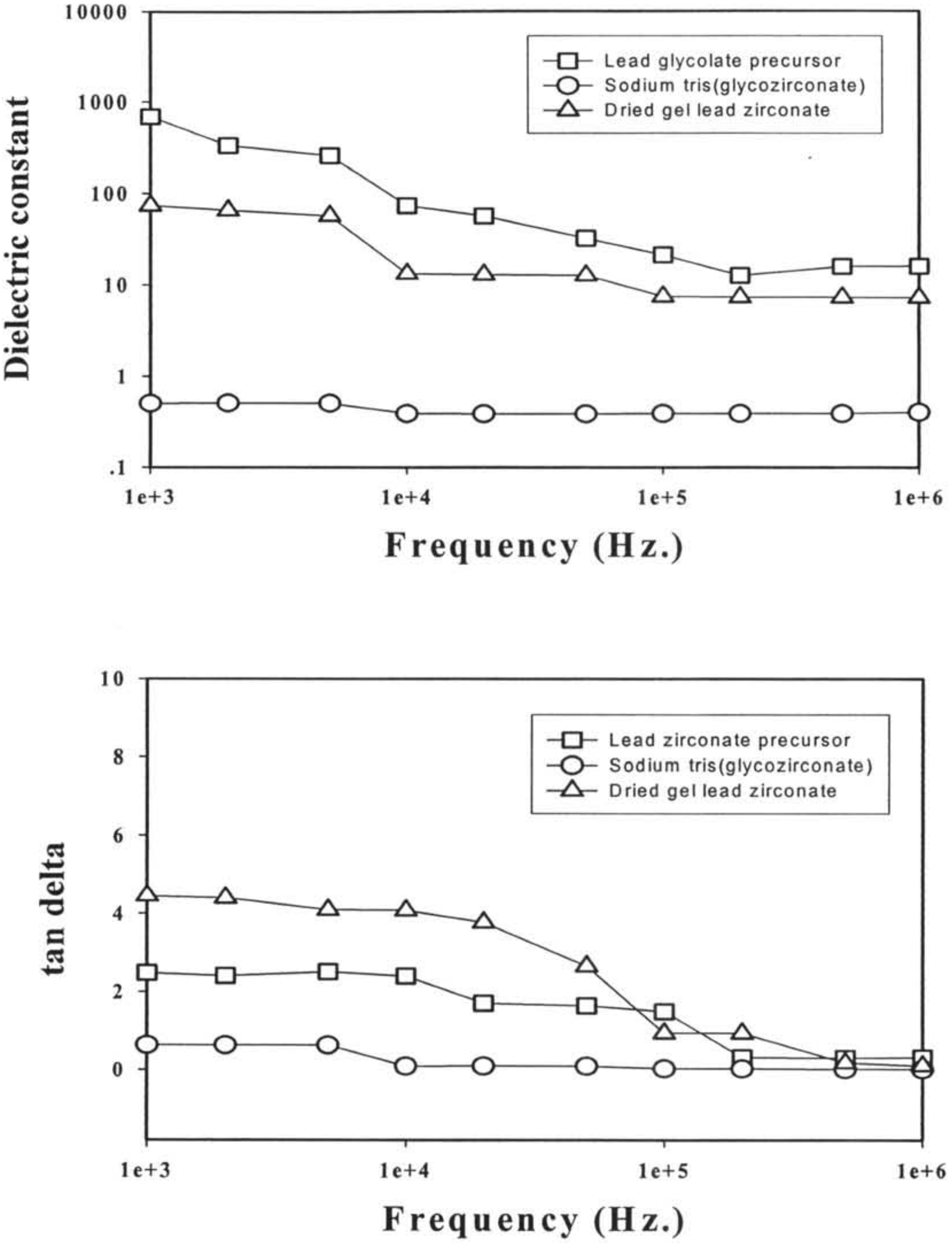


Figure 6.8 Dielectric constant and tan delta of lead glycolate precursor, sodium tris (glycozirconate), and dried lead zirconate gel vs. frequency measured at room temperature.

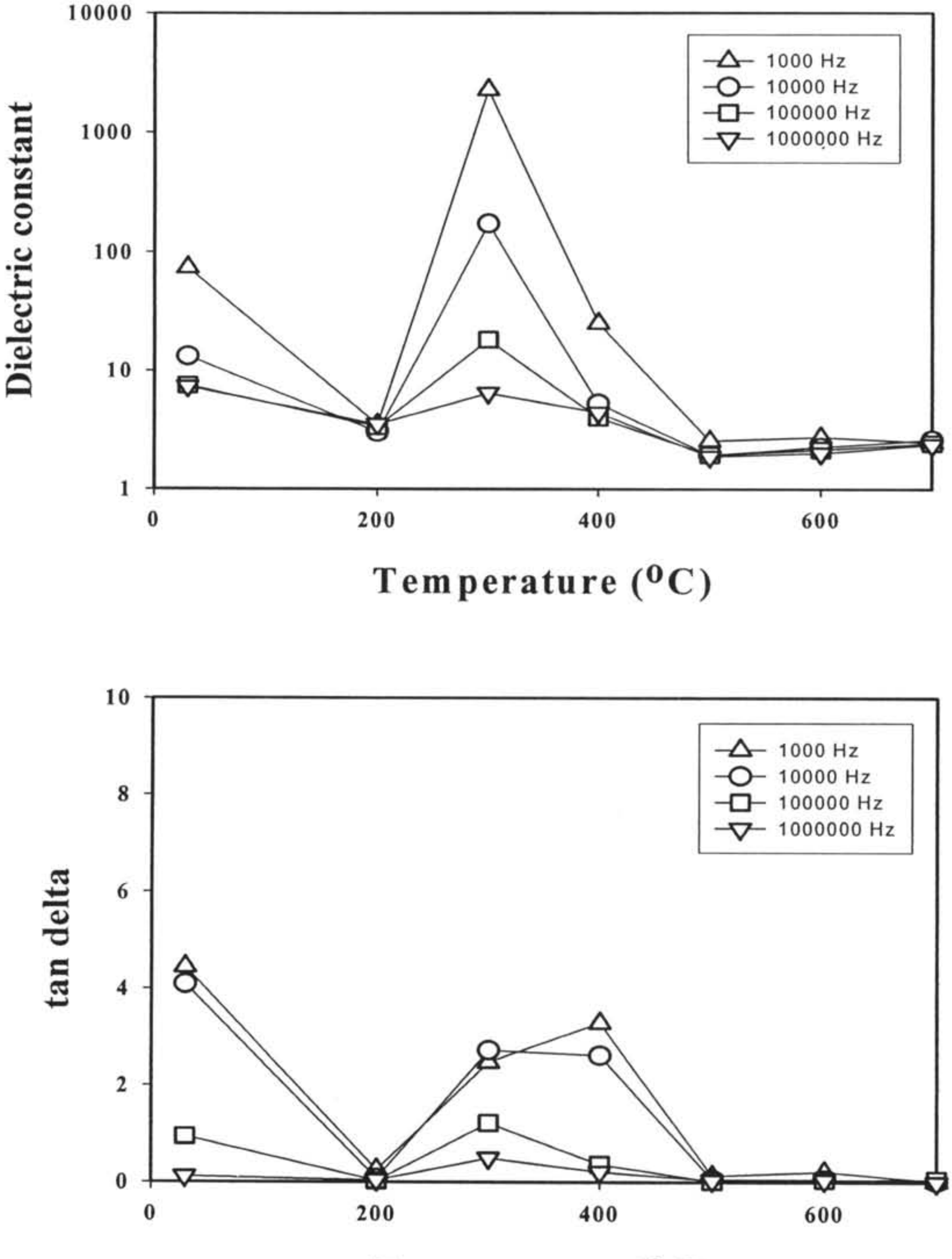


Figure 6.9 Dielectric constant and tan delta of calcined temperature lead zirconates at 200°, 300°, 400°, 500°, 600°, and 700°C for 1h. at various frequencies.