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A novel route to perovskite lead titanate from lead and titanium glycolates via the sol–gel process

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Pure perovskite lead titanate powder ($PbTiO_3$) is successfully produced via the sol–gel process using lead and titanium glycolates as starting precursors and has been synthesized by the oxide one spot synthesis process. The obtained lead titanate is of the tetragonal form of the perovskite phase, with high purity and nearly zero moisture content. From high-resolution mass spectra, the XRD technique, Raman-FTIR and TGA-DTA analysis, the lead–titanium glycolates undergo sol–gel transition through the formation of Pb–O–Ti bonds. From the SEM micrographs, the $PbTiO_3$ particle shape transforms from an agglomerate sphere to a needle and fiber-like shapes as the calcination temperature is varied above T_c. The corresponding molecular structural transformation, from the tetragonal form to the cubic form, occurs at 430 °C. The lead titanate powder calcined at 300 °C for 3 h has the highest dielectric constant and electrical conductivity values, namely 17470 and 1.83×10^{-3}, respectively. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: lead titanate; lead glycolate; titanium glycolate; ferroelectric and ferromagnetic materials

INTRODUCTION

Ferroelectric materials, especially polycrystalline ceramics, are promising for a variety of applications, such as sensors and actuators. Lead titanate is a kind of ferroelectric material having a permanent electric dipole moment whose complete or partial realignment can be reversed under appropriate conditions. Lead titanate 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, and a hydrothermal reaction.[1] Among those methods, the sol–gel process offers significant advantages: high purity, chemical homogeneity and controlled particle size, lower reaction temperature, and better control of molecular-level properties. One major disadvantage of the sol–gel process is the requirement for the expensive and moisture-sensitive alkoxide precursors used as starting materials.[2,3]

Li and Yao studied the synthesis of lead titanate powder derived from a hydrothermal treatment of lead acetate and titanium butoxide as the starting materials: they were mixed with poly-(*N*-vinylpyrrolidone) (PVP) and polyethylene glycol (PEG) as additives in an autoclave apparatus at the temperature ranging from 180 to 240 °C for 1–4 h.[4] Gelabert *et al.* studied a hydrothermal synthesis using lead titanate from chelated titanium and lead in alkaline aqueous solution in an autoclave at 200 °C for a period of 4–6 days. The products were identified as the tetragonal perovskite-type $PbTiO_3$.[5] Gurkovich and Blum prepared the transparent monolithic lead titanate by the sol–gel process. The reaction of lead acetate and titanium isopropoxide in metoxyethanol occurred at 124 °C. The structure of the alkoxide complex appeared to be a long chain of high molecular weight molecule, along with high viscosity. This resulted in the transformation from the tetragonal form to the cubic form of $PbTiO_3$, theoretically expected to occur at 490 °C.[6] Zeng *et al.* prepared nanocrystalline lead titanate by an accelerated sol–gel process. The gel formation was produced by lead acetate and titanium butoxide in $CH_3CHOHCH_3$ with a mole ratio of 1 : 1. The tetragonal perovskite structure $PbTiO_3$ with a particle size of 50 nm was prepared at 550 °C.[7] Tartaj *et al.* also prepared lead titanate by the sol–gel method using

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titanium tetrabutoxide in isopropanol and lead acetate in glacial acetic acid with a volume ratio of 1 : 1. Both solutions were mixed at room temperature under constant stirring for 24 h to ensure the formation of intermediate precursor phase based on Pb-O–Ti bonding.[8]

From previous studies, the sol–gel process appears to be an important route to produce lead titanate from lead and titanium alkoxide precursors, despite the fact that these precursors are moisture sensitive. Wongkasemjit and co-workers[9–12] demonstrated that, using the oxide one spot synthesis (OOPS) process, moisture-stable metal alkoxides can be successfully synthesized. Therefore, the objective of this work was to synthesize high purity lead titanate ($PbTiO_3$) via the sol–gel process using lead glycolate[11] and titanium glycolate[12] as the moisture-stable precursors. The effects of the Pb : Ti ratio (1 : 1, 1 : 2, 1 : 3, 1 : 4, 2 : 1, 3 : 1 and 4 : 1) and the calcination temperature on morphology, molecular transformation and the electrical properties were investigated.

EXPERIMENTAL

Materials

The starting raw materials, lead glycolate and titanium glycolate were synthesized using OOPS,[11,12] which produced less moisture-sensitive precursors. UHP-grade nitrogen, 99.99% purity, was obtained from Thai Industrial Gases Public Company Limited (TIG). Lead acetate trihydrate $Pb(CH_3COO)_2{}^{\bullet}3H_2O$, 99.5% purity, was purchased from Asia Pacific Specialty Chemical Limited (Australia). Titanium dioxide was purchased from Sigma-Aldrich Chemical Co. Ltd (USA). 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 and 200 °C before use. Triethylenetetramine (TETA) was purchased from Facai Polytech Co. Ltd (Thailand) and distilled under vacuum (0.1 mmHg) at 130 °C prior to use. Acetonitrile (HPLC-grade) was purchased from Lab-Scan Co. Ltd.

Instruments

The positive fast atom bombardment mass spectra (FAB^+-MS) were recorded on a Fison Instrument (VG Autospec-ultima 707E) using glycerol as a matrix, a cesium gun as indicator and cesium iodide (CsI) as a standard for the peak calibration. Fourier transform infrared spectra (FTIR) were recorded using a Vector 3.0 Bruker spectrometer with a spectral resolution of 4 cm^{-1} using ZnSe. 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 25–1200 °C temperature range. X-ray diffraction patterns (XRD) were taken and analyzed using a Philips Electronics analyzer (N.V. 1999) consisting of CuKα radiation ($\lambda = 0.154$ nm). Scanning electron micrographs (SEM) were obtained using a SEM Jeol-5200 electron microscope equipped with EDS for X-ray microanalysis. The percentages of chemical compositions of calcined powder were obtained using an X-ray analytical microscope (XGT 2000w, Horiba, Japan). The Raman spectra, recorded for powder samples, were obtained using a spectrometer (Labram HR 800, DU-420-OE-322).

Starting material preparation

Lead glycolate precursor[11]

Lead glycolate was synthesized via the OOPS process. A mixture of lead acetate trihydrate [$Pb(CH_3COO)_2{}^{\bullet}3H_2O$, 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) was heated at boiling point of EG (197 °C) under N_2 atmosphere in a thermostatted oil bath. The excess EG was slowly distilled off in order to remove water released from the reaction. After heating the mixture at 200 °C for 1 h, the solution color changed to yellow or golden brown. The reaction mixture was then cooled to obtain a crude precipitate product. The light bronze solid product was washed with acetonitrile and dried in a vacuum dessicator.

FTIR spectra were taken and analyzed: peaks appeared at 2778–2829 cm^{-1} ν(C–H), 1086, 1042 cm^{-1} ν(C–O–Pb bond), 573 cm^{-1} ν(Pb–O bond). ^{13}C-solid state NMR spectrum was taken; a single peak appeared at 68.6 ppm, representing ethylene glycol ligand. From the elemental analysis, data indicate 8.864% C and 1.392% H; these values are comparable to the expected values of 8.990% for C and 1.498% for H. From the FAB^+-MS analysis, we obtained an intensity of 55% at m/e equal to 801 for $[-(-PbOCH_2CH_2O-)_3-]$, an intensity of 25% at m/e equal to 595 for $[-OCH_2CH_2OPbOCH_2CH_2OPbO\ CH_2CH_2O- + H^+]$ and an intensity of 56% at m/e 505 for $[-CH_2OPbOCH_2CH_2OPb- + H^+]$. From the TGA thermogram, one decomposition transition occurred at 290–305 °C, corresponding to a 82.5% ceramic yield of $(-PbOCH_2CH_2O-)$ which is close to the calculated value of 83.50%.

Titanium glycolate precursor[12]

Titanium glycolate was synthesized via the OOPS process as well. A mixture of titanium dioxide (TiO_2, 0.025 mol, 2 g), TETA (0.0074 mol, 3.65 g), and ethylene glycol (EG added excess 25 cm^3) was stirred vigorously and heated at the boiling point of EG (197 °C) 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 spectra were taken and analyzed: peaks appeared at 2927–2855 cm^{-1} ν(C–H), 1080 cm^{-1} ν(C–O–Ti bond) and 619 cm^{-1} ν(Ti–O bond). ^{13}C-solid state NMR spectrum was taken: two peaks at 74.8 and 79.2 ppm occurred due to the crystalline phase of titanium glycolate.[12] From the EA analysis we obtained 28.6% C and 4.8% H. Data from FAB^+-MS indicated an intensity of 8.5% at m/e equal to 169 for

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$[Ti(OCH_2CH_2O)_2]H^+$, an intensity of 73% at *m/e* equal to 94 of $[OTiOCH_2]$ and an intensity of 63.5% at *m/e* equal to 45 belonging to $[CH_2CH_2OH]$. A TGA thermogram showed a sharp transition at 340 °C corresponding to a 46.95% ceramic yield of $Ti(OCH_2CH_2O)_2$.

Sol–gel preparation of lead titanate

Sol of the complex alkoxides mixture was prepared by mixing 2×10^{-2} g of lead glycolate (Pb content equal to 1.6×10^{-2} g) with 1.3×10^{-2} g of titanium glycolate (Ti content equal to 3.6×10^{-3} g) in a 0.1 M nitric solution (HNO_3). A white turbid solution was obtained. The sol–gel transition occurred within a few seconds as 1.0 M NaOH was added to bring pH to be in the range of 3–4 at room temperature. The gels were allowed to settle at room temperature (27 °C) for a period of 10 min and kept at 50 °C for 2 days, and we obtained the final product of a light yellow gel. The dried gels were subsequently calcined at 300, 400, 600, 800 and 1000 °C for periods of 1, 3 and 5 h, under oxygen atmosphere at the heating rate of approximately 10 °C/min.

Electrical properties characterization

The samples were prepared according to the ASTM B263-94 standard for electrical properties. Pellet samples were prepared as a thin disk 12 mm in diameter and 0.50 mm in thickness. In our experiment, the electrical properties were measured at frequencies between 10^3 and 10^6 Hz.

RESULTS AND DISCUSSION

Gel characterization

The gel formation of lead-titanium glycolates was initiated after adding 1.0 M NaOH into the lead glycolate and titanium glycolate nitric solution. The gel formed was turbid white. Figure 1 shows various FTIR peaks of the lead titanate gel: an OH band broad peak at 3650–3000 cm^{-1}, the asymmetric stretching of COO at 1540 cm^{-1}, and smaller peaks of ν(C–O–Ti) and ν(C–O–Pb) at 1080 and 1042 cm^{-1}, respectively, consistent with those previously reported.[12,13] The broad peak at 573–600 cm^{-1} can be identified as the Pb–O and Ti–O stretchings.[2,12,13] Figure 2 shows the FTIR spectra of samples with molar ratios of Pb : Ti at 1 : 1, 1 : 2, 1 : 3, 1 : 4, 2 : 1, 3 : 1 and 4 : 1. For the sample with the molar ratio Pb : Ti equal to 1 : 1, there are three distinct peaks: ν(OH) of the hydrolysis at 3400 cm^{-1}, ν(Pb–O–C) of the condensation at 1600 and 1400 cm^{-1}, indicating a complete gel formation.[7,18]

Figure 3 shows TGA thermograms between 25 and 1200 °C of the dried lead titanate gel. The total weight loss of the dried lead titanate gel was 25%. Therefore, ceramic yield of lead titanate was 75%, comparable to the calculated ceramic yield of 83.47%. The maximum value of weight loss occurred at 250–400 °C by exothermic reactions, consistent with the previously reported data.[2,14] The sharp exothermic peak at 182 °C resulted from the heat of vaporization of EG generated from the hydrolysis. The exothermic broad peak showed the Curie temperature occurring approximately at 430 °C; the expected Curie temperature of lead titanate was 490 °C.[6,8] In addition, there was an exothermic reaction of $PbO–PbTiO_3$ eutectic liquid existing at 872 °C, consistent with the theoretical phase diagram of $PbO–TiO_2$ at 838 °C.[8]

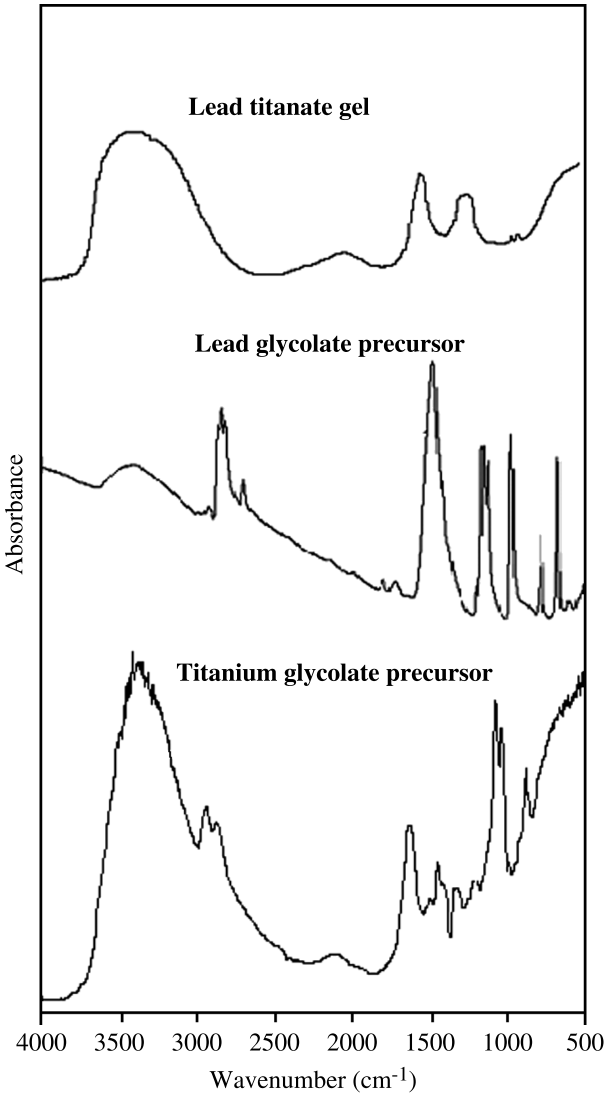

Figure 1 FTIR spectra of lead glycolate, titanium glycolate and dried lead titanate gel.

The mass spectroscopic data of the dried lead titanate gel are tabulated in Table 1. From the intensity peak positions identified with *m/e*, the ratio of atom mass per electron, we propose the structures present in the dried lead titanate gel (*m/e* 363, 9%; 321, 8%; 299, 18%; 115, 100%; and 92, 16%).

Lead titanate powder characterization

Figure 4 shows X-ray diffraction patterns of lead titanate samples of various calcination temperatures and times. For the sample of 300 °C at 1 h up to the sample 400 °C at 3 h,

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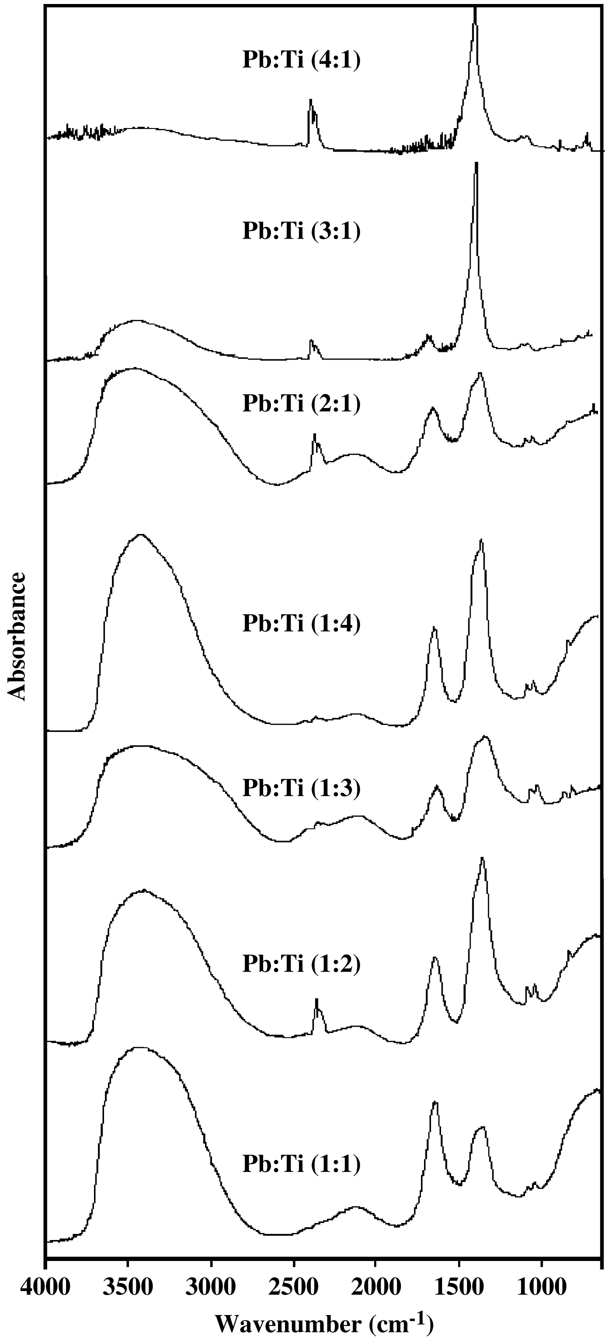

Figure 2 FTIR spectra of lead titanate samples prepared at various molar Pb–Ti ratios: 1 : 1, 1 : 2, 1 : 3, 1 : 4, 2 : 1, 3 : 1 and 4 : 1.

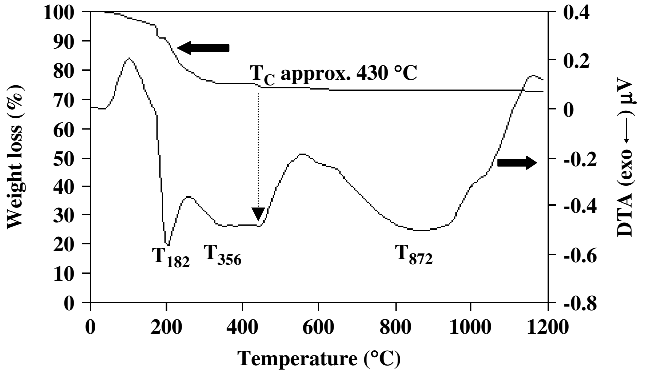

Figure 3 DTA and TGA thermograms of dried lead titanate gel.

Table 1. The proposed structures and fragmentation pattern of dried lead titanate gel by mass spectroscopy

m/e	Intensity (%)	Proposed structures
363	9.0	$-\text{O}-\underset{\mid}{\overset{\mid}{\text{Ti}}}-\text{O}-\text{Pb}-\text{O}-\text{CH}_2\text{CH}_2$
321	8.0	$-\text{O}-\underset{\mid}{\overset{\mid}{\text{Ti}}}-\text{O}-\text{Pb}- + 2\text{H}^+$
299	18.0	–Pb–O–Ti–O–C–
115	100.0	$-\text{O}-\underset{\mid}{\overset{\mid}{\text{Ti}}}-\text{O}- + 3\text{H}^+$
92	16.0	–O–Ti–O–C

the diffraction patterns indicate those of the tetragonal form of $PbTiO_3$,[1,2,7,17] a small amount of pyrochlore phase $PbTi_3O_7$ present,[1,15] and a large amount of residual amorphous phase. For the sample of 400 °C at 5 h up to the sample of 600 °C at 5 h, the diffraction patterns can be identified as the metastable pyrochlore phase[1,15] with a small amount of tetragonal form present.[1,2,7] For the sample of 800 °C at 1 h up to the sample of 1000 °C at 5 h, the diffraction patterns are of the perovskite cubic form.[8] These crystalline phases were identified according to the files of the Joint Committee on Powder Diffraction Standards (JCPDS). The JCPDS files used were 70–0746, 40–0099 and 70–1016 for the tetragonal form, the cubic form and the pyrochlore phase, respectively.

Figure 5(a, b) show Raman spectra of the calcined lead titanate samples obtained at various calcination temperatures and calcination times, respectively. In Fig. 5(a), there appears a peak at 290 cm^{-1} identifying the crystalline perovskite formation; the peak is more pronounced with increasing calcination temperature.[5,15,19,20] In Fig. 5(b), we compare the Raman spectra of samples at calcination temperature of 1000 °C at various calcination times of 1, 3 and 5 h. The peak at 290 cm^{-1} is more pronounced with increasing calcination time. The Raman shifts and spectra are nearly identical for the samples with calcination times of 3 and 5 h.

Figures 6 and 7 show SEM micrographs of the lead titanate powders at various calcination temperatures and times. Particles at the calcination temperature of 300 °C for 3–5 h appear to agglomerate. When they were calcined at higher temperatures and longer times, they changed from soft to hard aggregates, and the partially transformed structure appears to be of a needle-like shape. For the lead titanate samples calcined above 400 °C or higher than the Curie temperature, we can clearly observe the phase transformation

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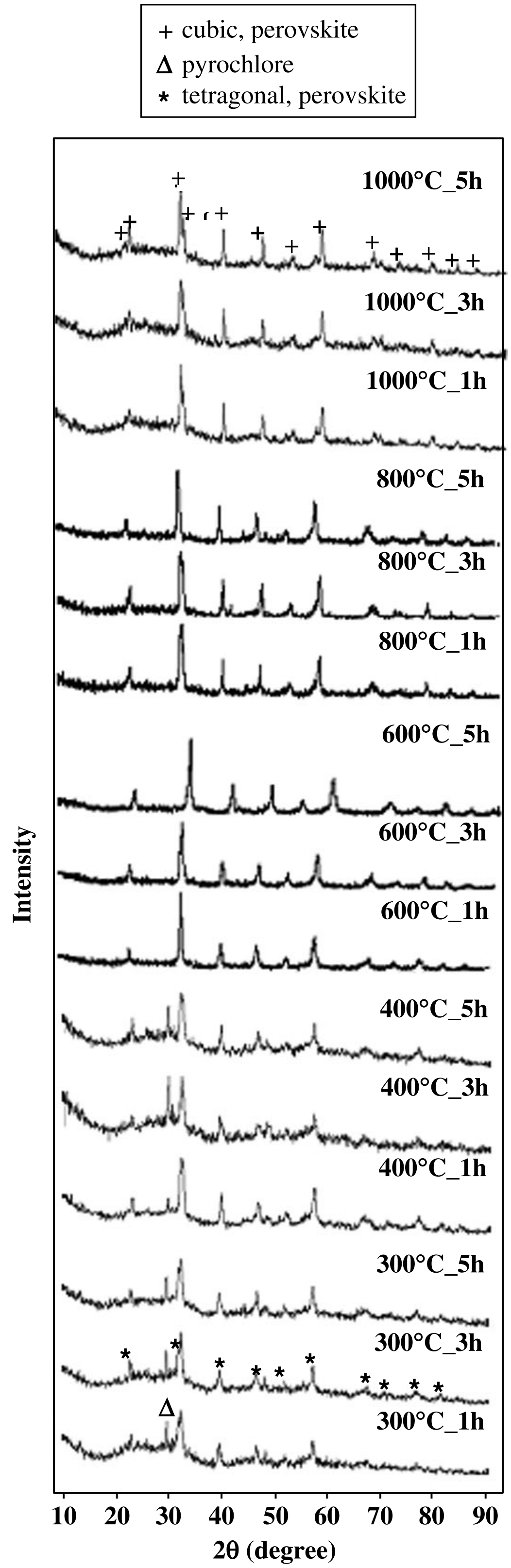

Figure 4 XRD diffraction patterns of calcined lead titanate powders at: 300, 400, 600, 800 and 1000 °C for 1, 3 and 5h (*, tetragonal perovskite; Δ, pyrochlore; +, cubic perovskite).

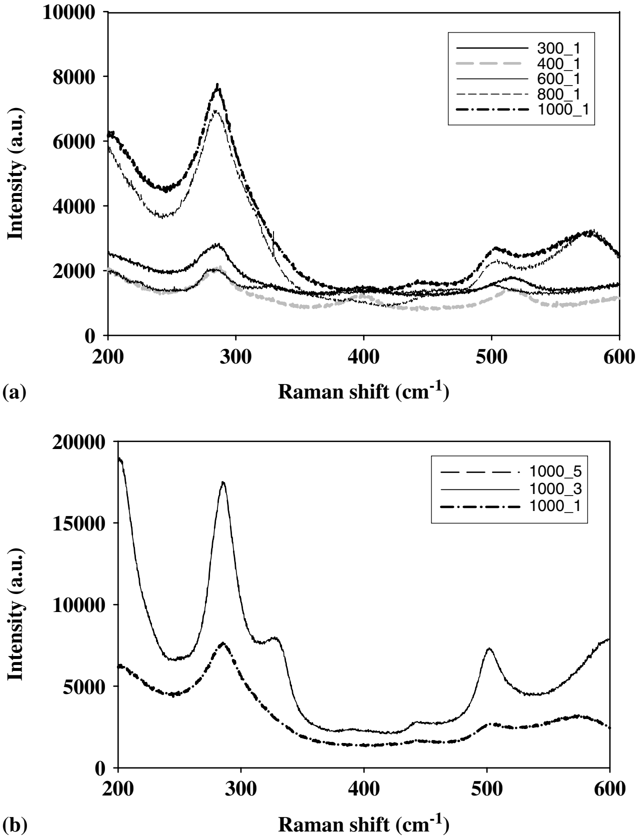

Figure 5 Raman spectra of lead titanates at: (a) 300, 400, 600, 800 and 1000 °C for 1 h; and (b)1000 °C for 1, 3 and 5 h.

from the tetragonal form (the spherical shape) to the cubic form (the needle shape), with increasing calcination temperature and time, as shown in Fig. 6. To confirm this finding, we present in Fig. 7 more SEM micrographs of the lead titanate powders calcined at various temperatures but at a fixed calcinations time of 3 h. They change from agglomerates into layers; the latter are the intermediate phase or the mixed phase between pyrochlore and perovskite, with increasing calcination temperature, and the microstructures of the cubic form are of needle-like or fiber-like, similar to those previously reported.[16]

The percentages of chemical compositions of calcined powders were analyzed by an X-ray analytical microscope and are summarized in Table 2. The experimental mole ratio of $PbO-TiO_2$ of the sample 300 °C at 3 h was 0.995 : 1, a value close to the calculated mole ratio of the lead titanate perovskite phase (1 : 1) as previously reported.[6,14]

Electrical properties of synthesized lead titanate

The electrical properties, namely the dielectric constant, the dielectric loss and the electrical conductivity, were measured as functions of calcination temperature, calcination time, and frequency, at 25 °C. In Table 3, we tabulate the data obtained at frequency equal to 1000 Hz. The dielectric constants of lead

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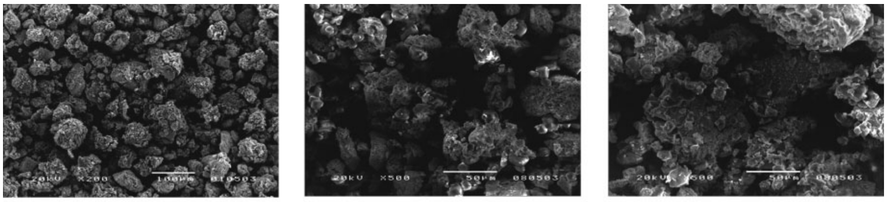
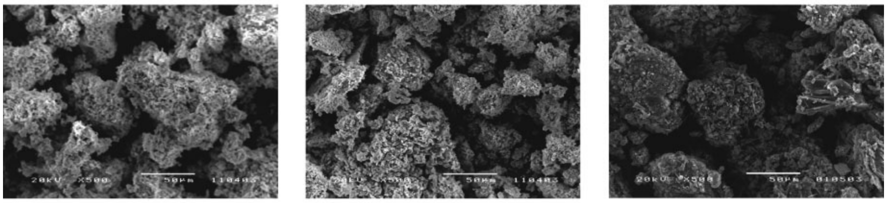
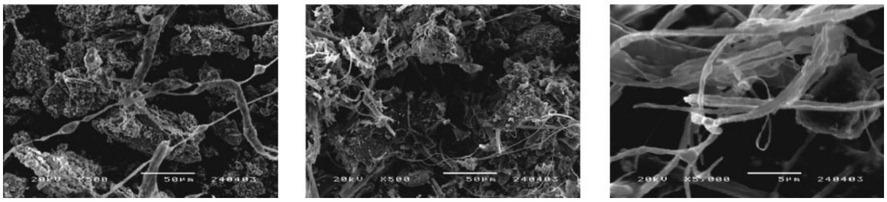


(a) 300°C_1h (a') 300°C_3h (a") 300°C_5h

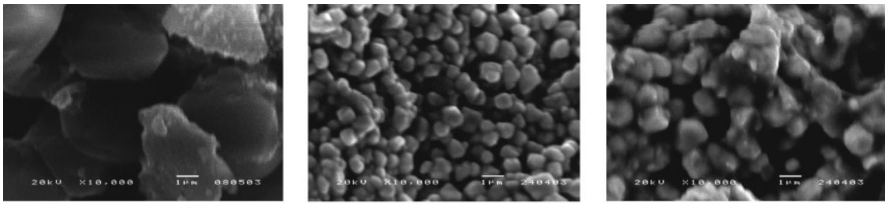


(b) 600°C_1h (b') 600°C_3h (b") 600°C_5h

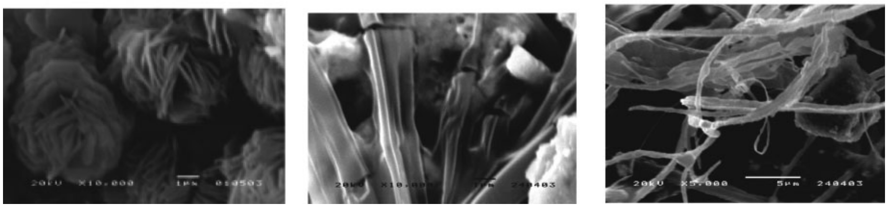


(c) 1000°C_1h (c') 1000°C_3h (c") 1000°C_5h

Figure 6. SEM micrographs (magnification = 500, size bar = 50 μm) showing the phase transformation of lead titanate calcined for 1 (column 1), 3 (column 2) and 5 (column 3) h at: (a) 300 °C; (b) 600 °C; and (c) 1000 °C.



(a) 25°C_3h (b) 300°C_3h (c) 400°C_3h



(d) 600°C_3h (e) 800°C_3h (f) 1000°C_3h

Figure 7. SEM micrographs (magnification = 10 000, size bar = 1 μm) showing agglomeration and crystal growth of lead titanate powders calcined from 25 °C (spherical shape) to 1000 °C (fiber-like): (a) 25 °C; (b) 300 °C; (c) 400 °C; (d) 600 °C; (e) 800 °C; and (f) 1000 °C for 3 h.

glycolate, titanium glycolate and dried lead titanate gel are 691, 15.7 and 1150, respectively. For the lead titanate 300 °C at 3 h powder, its dielectric constant attains a maximum value of 17 470. For the lead titanate 600 °C at 3 h powder, the dielectric constant is 11.6. For the lead titanate 800 °C_3h powder, the dielectric constant is 5.3. The high dielectric constant of the lead titanate 300 °C at 3 h powder is due to its tetragonal structure of the perovskite phase; the calcination temperature is below the Curie temperature of 430 °C at which we may expect to obtain ferroelectric behavior. On the other hand, for the lead titanate 600 °C at 3 h powder, its low dielectric constant is probably due to the mixed phases between $PbTiO_3$ and $PbTi_3O_7$, or a small amount of tetragonal form of the perovskite phase mixed with a larger amount of the pyrochlore

Table 2. The percentages of chemical compositions of calcined powder and mole ratio of Pb : Ti

Calcination temperature (°C) : time(h)	%Pb	%Ti	%O	%PbO	%TiO_2	Mole ratio, Pb : Ti
Ref. 14	—	—	—	72.90	26.30	0.994
Uncalcined	25.46	43.51	31.03	72.57	27.43	0.949
300 °C: calcined for 1 h	27.66	42.09	30.25	70.20	29.80	0.845
calcined for 3 h	68.22	15.89	15.89	73.49	26.51	0.995
calcined for 5 h	32.17	39.18	28.66	65.35	34.65	0.677
400 °C: calcined for 1 h	25.41	43.54	31.05	72.63	27.37	0.952
calcined for 3 h	73.86	12.25	13.89	79.57	20.43	1.397
calcined for 5 h	69.40	15.13	15.47	74.76	25.24	1.063
600 °C: calcined for 1 h	61.41	20.29	18.30	66.15	33.85	0.701
calcined for 3 h	68.22	15.89	15.89	73.49	26.51	0.995
calcined for 5 h	69.41	15.13	15.47	74.77	25.23	1.063
800 °C: calcined for 1 h	67.39	16.43	16.18	72.59	27.41	0.950
calcined for 3 h	74.34	11.94	13.72	80.08	19.92	1.442
calcined for 5 h	70.38	14.50	15.12	75.81	24.19	1.124
1000 °C: calcined for 1 h	67.69	16.23	16.07	72.92	27.08	0.966
calcined for 3 h	69.76	14.90	15.34	75.15	24.85	1.085
calcined for 5 h	67.36	16.45	16.19	72.56	27.44	0.949

Table 3. The electrical properties of lead glycolate, titanium glycolate and lead titanate synthesized were measured at 1000 Hz and 25 °C

Substances	Dielectric constant	Dielectric loss tangent (tan δ)	Conductivity $(\Omega m)^{-1}$
Lead glycolate	691	2.480	8.85×10^{-5}
Titanium glycolate	15.7	1.831	1.39×10^{-6}
Lead titanate, dried gel	1150	4.261	2.76×10^{-4}
Lead titanate, 300 °C, 1 h	2953	1.668	2.70×10^{-4}
Lead titanate, 300 °C, 3 h	17 470	1.467	1.83×10^{-3}
Lead titanate, 300 °C, 5 h	13 975	1.519	1.19×10^{-3}
Lead titanate, 400 °C, 1 h	3499	1.930	3.45×10^{-4}
Lead titanate, 400 °C, 3 h	12 160	1.502	9.80×10^{-4}
Lead titanate, 400 °C, 5 h	106	2.721	1.58×10^{-5}
Lead titanate, 600 °C, 1 h	6.10	2.916	9.52×10^{-7}
Lead titanate, 600 °C, 3 h	11.6	2.547	1.58×10^{-6}
Lead titanate, 600 °C, 5 h	3.7	1.964	3.76×10^{-7}
Lead titanate, 800 °C, 1 h	7.7	0.391	1.56×10^{-7}
Lead titanate, 800 °C, 3 h	5.3	0.287	8.33×10^{-8}
Lead titanate, 800 °C, 5 h	2.3	0.073	5.75×10^{-9}
Lead titanate, 1000 °C, 1 h	6.9	0.330	2.98×10^{-7}
Lead titanate, 1000 °C, 3 h	5.2	0.138	1.94×10^{-8}
Lead titanate, 1000 °C, 5 h	4.7	0.138	1.94×10^{-8}

phase, as previously shown by X-ray diffraction patterns in Fig. 4. For the lead titanate 800 °C at 3 h powder, its low dielectric constant is due to the cubic structure of the perovskite phase in which we may expect to obtain the paraelectric behavior. The corresponding dielectric loss tangent values for these three powders at 300, 600 and 800 °C for 3 h are 1.46, 2.54 and 0.287, respectively. The corresponding electrical conductivity values are 1.83×10^{-3}, 1.58×10^{-6} 8.33×10^{-8} S/m respectively. We can compare the electrical properties with those of previous reports; they obtained the lead titanate of the perovskite phase at 680 °C with corresponding electrical conductivity of about 10^{-5} S/m at 340 °C.[18]

Figure 8(a, b) shows the dielectric constant and the dielectric loss tangent values vs frequency of the precursors: lead glycolate, titanium glycolate and the dried lead titanate gel. Dielectric constants of the three samples decrease

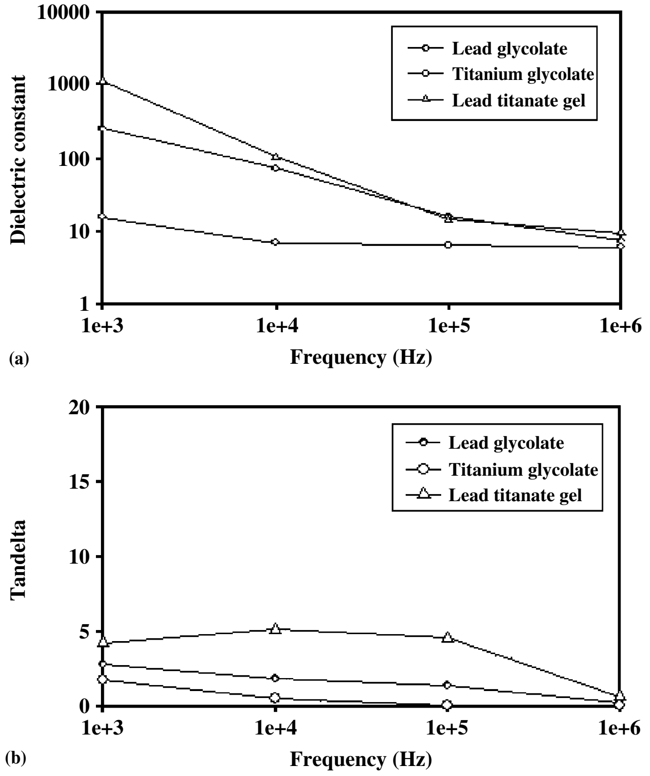


Figure 8 The dielectric constant and dielectric loss tangent (tan δ) vs frequency of lead glycolate, titanium glycolate and dried lead titanate gel measured at 25 °C.

monotonically with frequency in the range of 1000 to 10^6 Hz. The dielectric loss tangents remain of order one over the same frequency range.

Figure 9(a, b) shows the dielectric constant and the dielectric loss tangent values at various frequencies of the lead titanate powders calcined for 3 h at various calcination temperatures. The measurements were taken at 25 °C. The dielectric constant at 1000 Hz increases dramatically with calcination temperature below T_c; it reaches a value of 17 470 at the calcination temperature of 300 °C. Beyond T_c, it decreases with calcination temperature. Similar behavior occurs for other excitation frequencies; the dielectric constant increases with calcination temperature as long as it is below the Curie temperature. The likely explanation is phase transformation and structural changes occurring over this calcination temperature range. On the other hand, the dielectric loss tangents at any excitation frequencies decrease monotonically over the same calcination temperature range. The decreases in the dielectric constant and the dielectric loss tangents at high calcination temperature are expected due to melting of the PbO–TiO_2 perovskite phase in cubic form at 1285 °C, resulting in the PbO loss.[6,8]

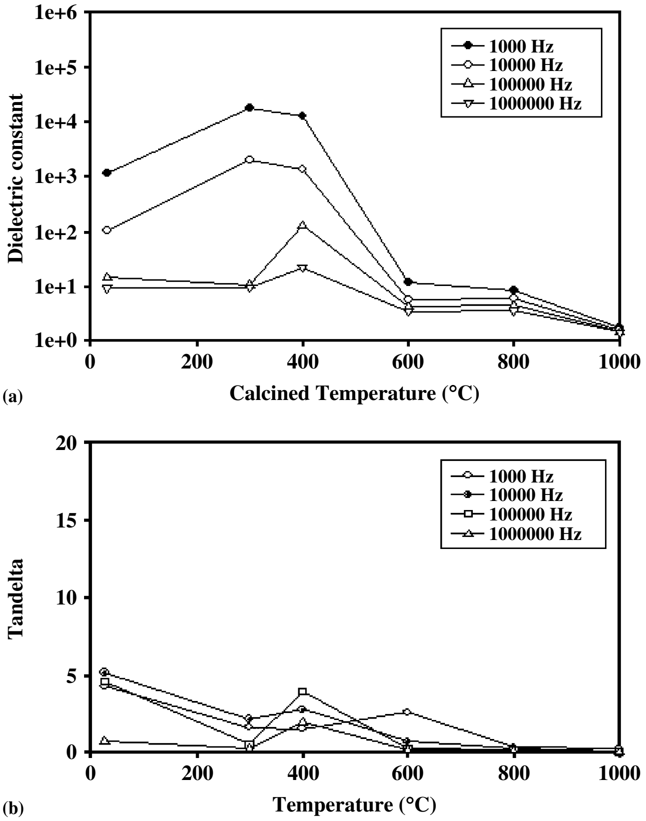
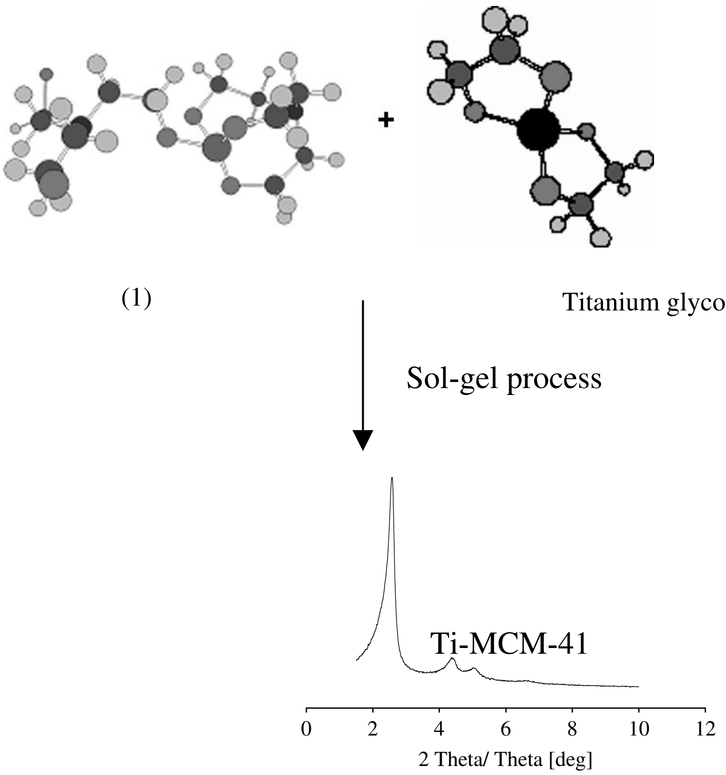


Figure 9 The dielectric constant and dielectric loss tangent (tan δ) measured at 25 °C of the lead titanate powders calcined at 300, 400, 600, 800 and 1000 °C for 3 h from 1000 Hz to 1 MHz.

CONCLUSIONS

The synthesis of lead titanate by the sol–gel process using lead glycolate and titanium glycolate as starting precursors gives a high-purity, inexpensive, easy to obtain and low moisture-sensitivity light yellow powder. The experimental stoichiometry value between Pb and Ti is 0.995 : 1, close to the calculated value of 1 : 1. The lead titanate gel was dried and calcined below T_c, 430 °C, in order to inhibit the structure transformation from the tetragonal form to the cubic form along with a change from ferroelectric behavior to paraelectric behavior. Highest dielectric constant of 17 470, dielectric loss tangent of 1.467 and electrical conductivity of 1.83×10^{-3} $(\Omega\ m)^{-1}$ were obtained for the powder sample calcined at 300 °C for 3 h, measured at room temperature and at 1000 Hz. The synthesized material appears to be a suitable candidate for using as an electronic-grade $PbTiO_3$ at low temperature compared with other methods or other starting materials such as the conventional, the solid state, the emulsion or the hydrothermal processes. In addition, our process avoids the harmful toxic lead since it is prepared below the lead melting temperature.



The dielectric constant measured at 25 °C of the lead titanate powders calcined at various temperatures for 3 h.

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