A Novel Route to Synthesis of Lead Glycolate and Perovskite Lead Titanate, Lead Zirconate, and Lead Zirconate Titanate (PZT) via Sol–Gel Process

นวัตกรรมของกระบวนการสังเคราะห์เลดไกลโคเลตและโครงสร้างแบบเพอรอฟสไกต์ของเลดไททาเนต เลดเซอร์โคเนต และ เลดเซอร์โคเนตไททาเนต ผ่านกระบวนการโซล-เจล

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ABSTRACT

The reaction of lead acetate trihydrate $Pb(CH_3COO)_2.3H_2O$ and ethylene glycol, using triethylenetetramine (TETA) as a catalyst, provides, in one step, an access to a polymer–like precursor of lead glycolate $[-PbOCH_2CH_2O-]$ via oxide one pot synthesis (OOPS). The lead glycolate precursor has superior electrical properties than lead acetate trihydrate, suggesting that the lead glycolate precursor can possibly be used as a starting material mixed with other precursors such as titanium glycolate and sodium tris (glycozirconate) to produce lead titanate, lead zirconate, and lead zirconate titanate by sol–gel transition process.

บทคัดย่อ

งานวิจัยนี้ได้ศึกษาการเกิดปฏิกิริยาระหว่างเลดอะซีเตดไตรไฮเดรต และเอทิลีนไกลคอลโดยใช้สารไตรเอทิลีนเตตระมีนเป็นคะตะลีสต์เพื่อใช้ในการผลิตสารตั้งต้นโพลิเมอร์คือเลดไกลโคเลต $[-PbOCH_2CH_2O-]$ ที่สำคัญชนิดหนึ่งต่อขบวนการนำไปใช้ในการสังเคราะห์ สารไดอิเลคตริกชนิดต่าง ๆ ได้แก่ สารเฟอร์โรไดอิเลคตริก สารแอนไทเฟอร์โรอิเลคตริกและสารเพียโซไดอิเลคตริกจากการสังเคราะห์ด้วยสารประกอบออกไซด์เพียงขั้นตอนเดียวที่เรียกว่า Oxide One Pot Synthesis (OOPS) ทำให้ได้สารตั้งต้นเลดไกลโคเลตมีสมบัติทางไฟฟ้าดีกว่าเลดอะซีเตดไตรไฮเดรต นอกจากนี้ยังสามารถนำไปใช้ผสมกับสารตั้งต้นชนิดอื่น ๆ เช่น ไททาเนียมไกลโคเลตและโซเดียมทรีสไกลโคเซอร์โคเนตเพื่อผลิตเลดไททาเนต เลดเซอร์โคเนตและเลดเซอร์โคเนตไททาเนต โดยผ่านกระบวนการโซล-เจลทรานสิชั่น

Key Words : OOPS, Sol–gel process, Dielectric materials
คำสำคัญ : OOPS กระบวนการโซล-เจล วัสดุไดอิเลคตริก

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Introduction

The semiconducting materials, such as ferroelectrics, antiferroelectrics, superconductor and piezoelectric products, show great potentials for using as sensors, actuators, transducers, electro-optic devices, thermistors, microelectro mechanical system (MEMS) applications (micromotors, microvalves, micropumps), PTC (positive temperature coefficient), acoustic transducer, binary ferroelectric memory, resistors and capacitors because of their good properties on dielectricity, pyroelectricity and piezoelectricity (Fang *et al*,1999; Lobmann *et al*.,1995; Paris *et al*., 1998; YXL, 1993). The most common and well-known electrical and semiconducting ceramic materials are lead titanate ($PbTiO_3$), lead zirconate ($PbZrO_3$), lead zirconate titanate (PZT or $Pb(Zr,Ti)O_3$) and lead/lanthanum zirconate titanate (PLZT or $(Pb,La)(Zr,Ti)O_3$). Many processes to produce these semiconducting ceramic materials include the sol-gel method, the chemical co-precipitation, the hydrother mal synthesis, the traditional solid state reaction of mixed oxides, the molten salt preparation, the solvothermal synthesis, the emulsion technique, and the complex polymerization (YXL, 1993; Fang *et al*., 2002; Hermandez *et al*., 2002; Bersani *et al*., 1995; Gurkovich *et al*., 1982; Palchik et al, 2000). The sol-gel process has an advantage over others in producing various shapes during the gel-state at low processing temperatures, e.g., monoliths, films, fibers and monosized powders along with compositional and microstructural controls (Brinker *et al*.., 1990). For conventional processes of producing semiconducting ceramics, the starting raw materials from metal alkoxide precursors require very high purity, but they are expensive and extremely moisture sensitive (Brinker *et al*., 1990).

Ferroelectric crystals necessarily possess both pyroelectric and piezoelectric properties. Many lose these polar properties at the transition or the Curie temperature T_c. A nonpolar phase above T_c is called paraelectric phase. Lead titanate and lead zirconate titanate are kinds of ferroelectric materials which have electric dipole moment which can be spontaneously polarized with reversibility [1,4-7]. Furthermore, ferroelectric can be used as biosensor such as piezo-sensing devices and biosensors for urea, glucose, DNA, immune cholesterol (Brinker *et al*., 1990). Lead zirconate is an antiferroelectric material having a non-permanent electric dipole moment whose complete or partial realignment can be reversible under appropriate conditions. Lead zirconate can show a phase switching from the antiferroelectric phase to the ferroelectric phase by applying electric field or raising temperature. The methods required for the synthesis of alkoxy derivatives of an element generally depend on its electronegativity and electron configuration. The chelating nature of the glycol and the coordinative saturation achieved by the central atoms in the final products appear to be the main factor for their hydrolytic stability to retard the hydrolysis and condensation reaction rates in order to form homogeneous gels rather than precipitates (Kakihana *et al*., 1997). Other work reported metalloglycolates formed from alkaline glycol such as aluminium, silicon, titanium, and magnesium-aluminium (Yang *et al*., 2001; Day *et al*., 1996; Brinker *et al*., 1986). Specifically, (Archer *et al*., 1996) studied the role of precursor segregation in the formation of the perovskite phase $PbTiO_3$ using either lead oxy glycolate $Pb(OCH_2CH_2O)_2$ or lead phenoxy glycolate compounds. The lead precursors were synthesized by refluxing the lead carbonate with an appropriate carboxylic acid in water.

From previous studies, the sol-gel process appears to be the mildest method to produce lead titanate, lead zirconate, lead zirconate titanate. In an all-alkoxide sol-gel process, alkoxides of the constituent elements show different reactivities toward water so that the preparation of multicomponent homogeneous systems is difficult. The high cost of the alkoxide reagents and the need to work under inert atmospheres are major disadvantages of this system. Inorganic and organic salts have also been used for the sol-gel processing of multicomponent systems when the use of constituent alkoxides become difficult or unnecessary. Many researches by Wongkasemjit *et al.*, group reports have demonstrated that using the Oxide One Pot Synthesis (OOPS) process, moisture stable metal alkoxides can be successfully synthesized. Therefore, the aim of this study is to synthesize high purity lead titanate, lead zirconate and lead zirconate titanate (PZT) via the sol-gel process using lead glycolate, titanium glycolate and sodium tris (glycozirconate) precursors from the OOPS process. We also investigate the influence of calcination temperature and time on physical and chemical properties; i.e., morphology, phase transformation, and electrical properties.

Experiment

Materials

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) and used as received. Titanium dioxide was purchased from Sigma-Aldrich Chemical Co., Ltd. (USA). Zirconium (IV) hydroxide $Zr(OH)_4$ containing 88.8% ZrO_2 was purchased from Aldrich Chemical Co., Inc. (USA). Ethylene glycol (EG) was purchased from Farmitalia Carlo Erba (Barcelona) or Malinckrodt Baker, Inc. (USA). 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 was purchased from Lab-Scan Co., Ltd.

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

Precursor Synthesis

Lead Glycolate [16]

Lead glycolate was synthesized via the OOPS process. 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) acted as a catalyst when heated at the boiling point of EG under N_2 in a thermostated oil bath. The excess EG was slowly distilled off as to remove water liberated from reaction. After heating at 200°C for 1 h, the solution color changed to be yellow or golden brown. The reaction mixture was cooled to obtain a crude precipitate product followed by filtration with acetonitrile. The light bronze solid product was obtained and dried in a vacuum dessicator (0.1 mm Hg) at room temperature and characterized using FTIR,

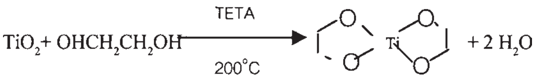
^{13}C-NMR,FAB+-MS, TGA, pycnometer and Impedance Analyzer.

$$3Pb(CH_3COO)_2.3H_2O + HOCH_2CH_2OH \xrightarrow[200^\circ C]{TETA} \text{-} [\text{-}PbOCH_2CH_2O\text{-}]_3\text{-} + 9H_2O + 2CH_3COOH$$

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

Titanium Glycolate [15]

Titanium glycolate was also synthesized via the OOPS process. A mixture of titanium dioxide (TiO$_2$, 0.025 mol, 2 g) and TETA (0.0074 mol, 3.95 g) mixed with ethylene glycol (EG added excess 25 cm3) was stirred vigorously and heated at the boiling point of EG for 24 h, followed by separating the unreacted TiO$_2$ from the solution part. The excess of EG and TETA were removed by the vacuum distillation to obtain a crude precipitate. The white solid product was washed with acetonitrile and dried in a vacuum dessicator before characterization using FTIR, TGA.



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

Sodium tris (glycozirconate) [12]

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

$$Zr(OH)_4 + NaOH + HOCH_2CH_2OH \xrightarrow{200^\circ C} Na_2Zr(C_2H_4O_2)_3$$

FTIR bands were observed were: 3000-3700 cm^{-1} ν(O-H) w, trace of water absorbed in the product, 1600 cm^{-1} the (O-H) bending vibration of the water of hydration, 2873 and 2939 cm^{-1} the ν(C-H), 1200-1400 cm^{-1} of methylene groups, 1090 cm^{-1} the (Zr-O-C) stretching vibration mode, 880 cm^{-1} the (C-C) bond deformation, 613 cm^{-1} the (Zr-O) stretching. TGA showed one major thermal decomposition ranging from 350°C to 545°C. The percentage ceramic yield of the product was 58.41% which is close to the theoretical ceramic yield 58.33%. EA results are 22.41% (Carbon) and 4.23% (Hydrogen) which are close to the theoretical C and H content 22.70 and 3.78 respectively. ^{13}C-NMR found a single peak at 62.6 ppm belonging to the symmetrical carbon chelated glycolate ligand (CH_2-O-Zr).

Instrument

The positive fast atom bombardment mass spectra (Maldi-tof-MS) were recorded on a Bruker Instrument (Polymer TOF-Bruker) 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°C-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 a Phillip Electronic 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). Electrical properties were measured and obtained using an impedance analyzer (1kHz.-1000kHz.).

Methodology

Lead Titanate Preparation via Sol-Gel: $PbTiO_3$

The structure of lead titanate $PbTiO_3$ was composed of mol ratio Pb:Ti:O equal to 1:1:3. A mixture of lead glycolate mixed with titanium glycolate alkoxide precursor was prepared with 1 mol of Pb(II) : 1 mol of Ti(IV). The mixture was mixed into 0.1 M nitric solution (HNO_3) to obtain complex alkoxide sol which was white turbid solution. The transition from sol to gel occurred by adding 1.0 M sodium hydroxide solution (NaOH) to adjust pH to a value 3-4 at room temperature within a few minute. The molar ratios of Pb:Ti between lead glycolate and sodium tris (glycozirconate) precursors at 1:1; 1:2; 1:3; 1:4; 2:1; 3:1 ;4:1 were selected to study the complete sol-gel formation. The gels derived from the complex alkoxide of lead-titanium glycolate were allowed to settle at room temperature and were dried at 50°C within 1-2 days. The color of dried gel was light yellow. After that, the dried gels were calcined at 300°C, 400°C, 600°C, 800°C and

1000°C for 1, 3 and 5 h. Sol-gel products were characterized by FTIR, ^{13}C-NMR, SEM, XRD, Raman, TGA, and impedance analyzer.

Lead Zirconate Preparation via Sol-Gel : $PbZrO_3$

The structure of lead zirconate $PbZrO_3$ was composed of mol ratio Pb:Zr:O equal to 1:1:3. Sol of complex alkoxide mixture was prepared by mixing lead glycolate in a 0.1 M nitric solution (HNO_3) with sodium tris (glycozirconate) dissolved in water. The white turbid sol formation was obtained when they were poured to react together. The sol to gel transition occurred within a few second when adding a little amount of water to adjust pH in the range of 8-9 at room temperature. The molar ratios of Pb:Zr between lead glycolate and sodium tris (glycozirconate) precursors at 1:1; 1:2; 1:3; 1:4; 2:1; 3:1 ;4:1 were selected to study the completely sol-gel formation. The gels were allowed to settled at room temperature and dried at 50°C for 2 days to finally obtain a light yellowed gel. The gels were calcined at 200°C, 300°C, 400°C, 500°C, 600°C and 700°C for 1, 2 and 3 h. The dried gels were charaterized by FTIR, ^{13}C-NMR, SEM, XRD, Raman, TGA, and impedance analyzer.

Lead Zirconate Titanate Preparation via Sol-Gel: $Pb(Zr_x,Ti_{1-x})O_3$/PZT

The structure of lead zirconate titanate $Pb(Zr_x,Ti_{1-x})O_3$ was composed of the mol ratio Pb:Zr,Ti:O equal to 1:1:3. Sols of complex alkoxide mixture were prepared by mixing lead glycolate and titanium glycolate in a 0.1 M nitric acid solution (HNO_3) with sodium tris (glycozirco nate) dissolved in water. The white turbid sol formation occurred when they reacted with each other. The sol to gel transition occurred within a few minute when adding a little amount of water to adjust pH in the range of 5-6 at room temperature. The molar ratios of Pb:Zr:Ti among lead glycolate, sodium tris (glycozirconate), titanium glycolate precursors at 1:0.8:0.2; 1:0.7:0.3; 1:0.6:0.4; 1:0.5:0.5; 1:0.4:0.6; 1:0.3:0.7; 1:0.2:0.8 were selected to study the complete sol-gel formation. The gels were allowed to settle at room temperature and dried at 50°C for 2 days to finally obtain a browned gel. The gels were calcined at 200°C, 300°C, 400°C, 500°C, 600°C, 700°C and 800°C for 1, 2 and 3 h. The dried gels were characterized by FTIR, ^{13}C-NMR, SEM, XRD, Raman, TGA, an impedance analyzer.

Results and Discussions

$PbCH_3(COO)_2.3H_2O + OHCH_2CH_2OH + TETA \longrightarrow$ X (Pb precursor)

$Zr(OH)_4 + NaOH + OHCH_2CH_2OH + TETA \longrightarrow$ Y (Zr precursor)

$TiO_2 + OHCH_2CH_2OH + TETA \longrightarrow$ Z (Ti precursor)

$X + Z \longrightarrow$ PT precursor

$X + Y \longrightarrow$ PZ precursor

$X + Y + Z \longrightarrow$ PZT precursor

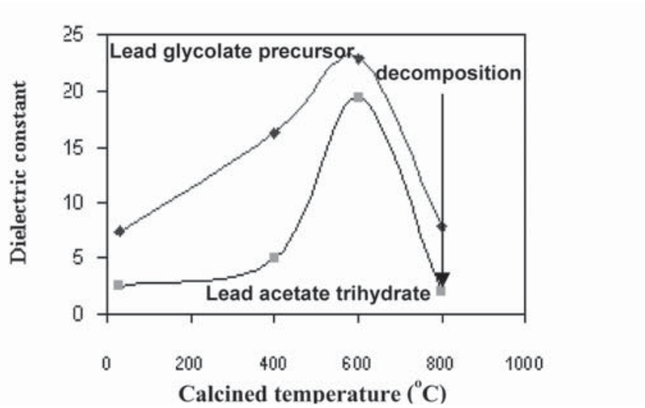


Figure 1 The dielectric constant of lead acetate trihydrate and lead glycolate precursor.

Figure 1 shows dielectric constant values of lead glycolate and lead acetate trihydrate. The dielectric constant, resistivity, and conductivity of lead glycolate values are 7.42-22.96, 1.3-2.3x10^{11} ohm.m and 4.28-7.99 x 10^{-12} ohm^{-1}.m^{-1}, at 10^{6} Hz, respectively. The corresponding values of dielectric constant, resistivity, and conductivity for lead actate trihydrate are 2.5-19.31, na-2.3x10^{11} ohm.m and na-4.40 x 10^{-12} ohm^{-1}.m^{-1}, at 10^{6} Hz., respectively. Evidently, the electrical properties of lead glycolate are superior than those of lead acetate trihydrate at all temperatures investigated. The decreases in values at 800°C are probably due to the decomposition of lead oxide occurring at high temperature.

Thermal behavior was investigated by a TGA measurement. The decomposition profile and ceramic yield of the proposed product are shown in Figure 2. The thermal decomposition of the glycol ligand occured in the range of 290°C-305°C. The final ceramic yield obtained was 82.50%; this is 1% lower than the theoretical yield value of 83.50% due the evaporation of some lead oxide at around 800°C.

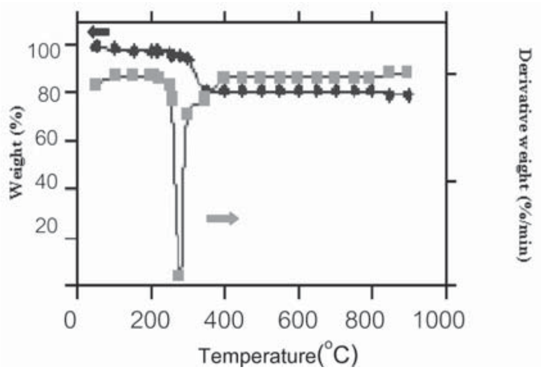


Figure 2 TGA curve of lead glycolate precursor

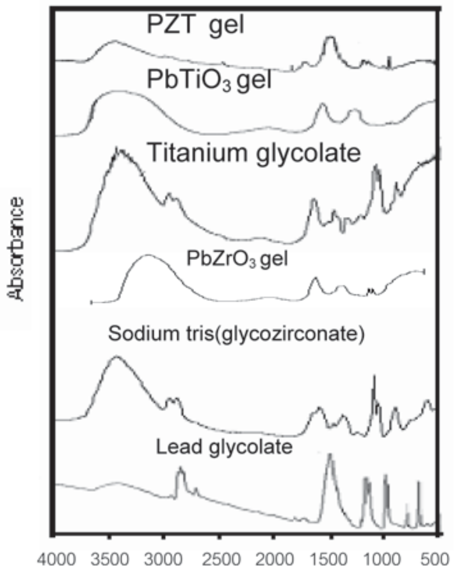


Figure 3 FTIR of precursors and gel samples

FTIR sprectra of lead zirconate tiatanate dried gel (PZT), lead glycolate, and sodium tris (glycozirconate) precursor are shown in Figure 3. For the PZT gel spectrum, there are a visible broad peak at 3500 cm^{-1} (O-H), smaller peaks at 1725, and 1630 cm^{-1} (νC-O), and a peak at 1085 cm^{-1} (νC-O-Pb). The broad peak at 783 cm^{-1} can be identified as the Pb-O-Zr stretching.

Table1 and figure 4 show the dielectric constants and dielectric loss tangents of the starting precursors and lead zirconate titanate dried gel as functions of frequency at 27°C. It can be seen that the lead zirconate titanate powder calcined at 400°C for 1h possesses the highest dielectric constant at 1000 Hz and the highest electric conductivity; namely, 10,190 and 0.803 x 10^{-3} S/m, respectively. The dielectric constants and the dielectric loss tangents of materials generally decrease with increasing frequency, indicative of the polarization mechanisms involved: the electronic, atomic, dipole, and interfacial polarizations. For the sample PZT (400_1h), 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 10,190 and 1.513, respectively as expected to occur close to the Curie temperature of 400oC. We may compare our data of our synthesized $Pb(Zr_{0.5}Ti_{0.5})O_3$ or PZT4 with the data of other previous workers who obtained dielectric constant of 8600 and 1050, measured at 1000 Hz. and at room temperature[23,24].

Table 1 Electrical properties of samples measured at room temperature, 1000 Hz.

samples	Dielectric constant	Dielectric loss tangent (tanδ)	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 gel lead titanate	1150	4.261	2.76×10^{-4}
Dried gel lead zirconate	73.76	4.448	1.516×10^{-4}
Dried gel PZT	9.832	0.405	9.980×10^{-8}
PZT (400_1h)	10190	1.513	0.803×10^{-3}

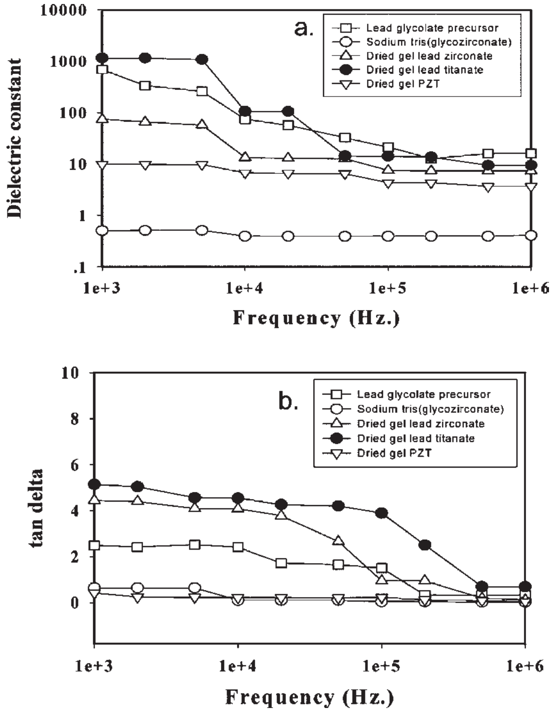


Figure 4 Dielectric constant and tan delta vs. frequency measured at room temperature.

Raman spectra of lead glycolate precursor, sodium tris (glycozirconate) precursor, titanium glycolate precursor, lead zirconate dried gel, lead titanate dried gel and lead zirconate titanate dired gel are shown in Fig.5 where the spectrum of the latter shows a broad band indicating its amorphous structure. Figure 5 expressed Raman spectra of lead zirconate titanate $Pb(Zr_xTi_{1-x})O_3$ at room temperature confirming by report [6].

^{13}C-NMR spectra of lead glycolate, sodium tris (glycozirconate), titanium glycolate, lead zirconate dried gel, lead titanate dried gel, and lead zirconate titanate dried gel are shown in Fig. 6. All of spectra expressed peak of ethylene glycol ligand at approximately 69 ppm. Our results are confirmed by the report [8-10,14].

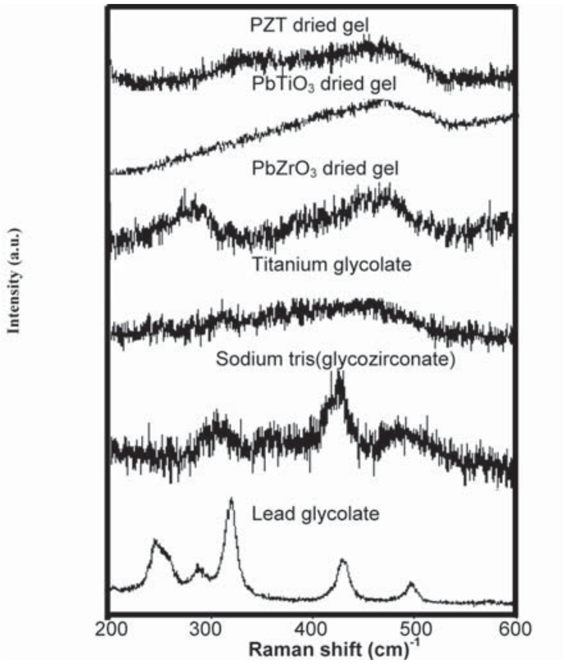


Fig 5 Raman spectra of samples

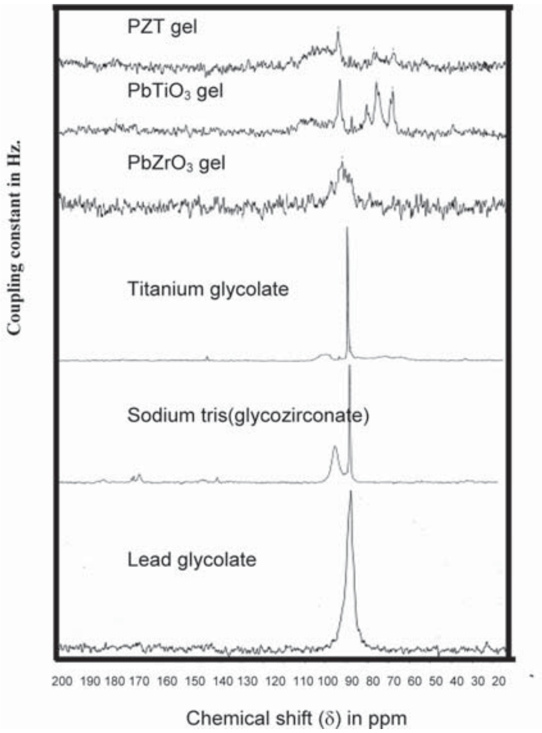


Fig 6 Solid ^{13}C NMR of samples

Conclusions

The lead glycolate precursor was successfully with a very high yield. The product has high purity and it is moisture stable as shown by TGA data. The FTIR result shows the Pb-O-C bonds while the NMR data give only a single peak of ethylene glycol ligand. FAB+-MS gives the molecular peak of a trimer $-[-PbOCH_2CH_2O-]_3-$. The percentages of carbon (8.864) and hydrogen (1.392) contents in the product are close to the theoretically calculated values (8.990%C and 1.498%H) respectively [16]. Since the lead glycolate is more stable, it is soluble in most acid solutions, except for nitric acid. With its small particle size (36.80 micron), lead glycolate is useful for selectively mixing with other precursors, such as titanium glycolate and zirconium glycolate, to produce lead titanate, lead zirconate and lead titanate zirconate (PZT). From the electrical properties and the microstructures at high temperature, we can summarize the lead glycolate precursor could be used as a possible starting material for ferroelectric, anti-ferroelectric, and piezoelectric materials [22].

The synthesis of lead titanate by the sol-gel process using lead glycolate and titanium glycolate as starting precursors gives a high purity and low sensitivity to moisture light yellow color 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 of 430°C in order to inhibit the tetragonal transform to the cubic form of perovskite phase which induces a change from the ferroelectric behavior to the paraelectric behavior. The 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. Our synthesized material appears to be a suitable candidate for using as an electronic-grade $PbTiO_3$.

The synthesis of lead zirconate by the sol-gel process using lead glycolate and sodium tris (glycozirconate) as starting precursors gave the same results as those of lead titanate; the product is of high purity, low moisture sensitivity, and of light yellow color powder, but it has the antiferroelectric behavior. The experimental stoichiometry value between PbO and ZrO_2 is 0.9805:1.00, close to theoretically calculated 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 2,267, electrical 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 can be used as an antiferroelectric-grade $PbZrO_3$.

Moreover, the synthesis of lead zirconate titanate by the sol-gel process using lead glycolate, sodium tris (glycozirconate) and titanium glycolate as starting precursors gave a product of high purity, low moisture sensitivity, and light yellow color powder as well. The experimental stoichiometry value between PbO, ZrO_2 and TiO_2 is 1.00:0.521:0.479, close to theoretically calculated value of $Pb(Zr_{1-x}Ti_x)O_3$ (1:0.5:0.5). The lead zirconate titanate gel was dried and calcined below limiting curve of T_c in order to prevent the structural change from the tetragonal or orthorhombic forms to the cubic form of the perovskite phase. The highest dielectric constant of 10,190, electrical conductivity of 0.803×10^{-3} $(\Omega.m)^{-1}$, and low dielectric loss tangent of 1.513 measured at 1000 Hz. were obtained from the $Pb(Zr_{0.5}Ti_{0.5})O_3$ calcined at 400°C for 1 h. Dielectric constant and conductivity decreased with calcination time and temperature when it was above the limiting curve of T_c. Our synthesized materials appear to be a suitable material for many applications as an piezoelectric-grade $Pb(Zr_{0.5}Ti_{0.5})O_3$ as well.

Suggestions

The future works are preparation of PZT, $PbZrO_3$, $PbTiO_3$ thin film and thick film, including their properties. Synthesis of doping metal on PZT, i.e. Ba, Ca, Mn, Sr to improve their electrical properties. Further more, preparation sol of $PbTiO_3$, $PbZrO_3$, $Pb(Zr,Ti)O_3$/ PZT nanofiber and their properties.

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