

SOL-GEL PROCESS FOR THE MANUFACTURING OF TRANSLUCENT LEAD ZIRCONATE TITANATE GEL-MONOLITH

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ABSTRACT

Translucent Lead Zirconate Titanate (PZT) gel-monolith was prepared by partially hydrolyzing metal alkoxides solution which modified with acetylacetonate (acacH). Metal alkoxides, lead di-*i*-propoxide, zirconium tetra-*n*-butoxide and titanium tetra-*i*-propoxide were used as starting materials. In Infrared spectra for the translucent monolithic gel after aging at room temperature for several days or drying at 90 °C for 18h, the most significant feature is the presence of band at around 1554 cm⁻¹ which can be assigned to the ν (C-O) and ν (C-C) vibrations of acetylacetonate group coordinated to the metal cations Ti and Zr. The diffraction peaks of PbO were found after heating at 300 °C for 2h. After heating at 450 °C for 2 h, diffraction peaks of pyrochlore Pb₂Ti₂O₆ and perovskite PZT phase were observed. The diffraction peaks of PbO and pyrochlore phase disappeared after heating at 600 °C, and tetragonal perovskite phase was stable up to 1000 °C. The diffraction peaks of perovskite phase were also found after heating at 430 ° for 24 h. The density of the compacted pulverized gel after heating at 1000°C for 30 min. was 6.9 g/cm³, about 86% of the theoretical value.

INTISARI

Translucent monolith gel Timbal Zirko-nat Titanat (PZT) dibuat dengan menghidrolisa sebagian dari larutan metal alkoksida yang telah dimodifikasi dengan acetylaceton(acacH). Bahan dasar metal alkoksida yang digunakan adalah, timbal di-*i*-propoksida, zirkonium tetra-*n*-butok-sida dan titanium tetra-*i*-propoksida. Ciri-ciri penting dari spetra infra merah untuk translucent monolith gel yang telah didiamkan pada suhu kamar selama beberapa hari atau dikeringkan pada 90 °C selama 18 jam, adalah adanya puncak sekitar 1554 cm⁻¹ yang mana dapat menentukan vibrasi-vibrasi ν (C-O) dan ν (C-C) dari gugus

acetylacetonate yang terkoordinasi pada kation Ti dan Zr. Setelah dipanaskan pada suhu 300 °C selama 2 jam puncak-puncak difraksi PbO diperoleh. Setelah dipanaskan pada suhu 450°C selama 2 jam difraksi puncak-puncak dari fasa pyrochlore Pb₂Ti₂O₆ dan fasa perovskite PZT teramati. Setelah dipanaskan pada suhu 600 °C, difraksi puncak-puncak dari PbO dan fasa pyrochlore hilang dan fasa tetragonal perovskite tetap stabil sampai pemanasan 1000 °C. Difraksi puncak-puncak fasa perovskite juga didapat setelah pemanasan pada suhu 430°C selama 24 jam. Berat jenis dari bubuk gel yang dipadatkan setelah pemanasan pada 1000°C selama 30 menit adalah 6.9 g/cm³, sekitar 86% dari berat jenis secara teoritis.

INTRODUCTION

Metal oxide ceramics of complex stoichiometry are widely used in the electronic industry for applications including capacitors, transducers, or substrates. The PZT ceramics are important members of the class of piezoelectric ceramics [1]. They are attractive materials because of their excellent electrical properties, such as high dielectric constant, high Curie temperature and high electromechanical coupling coefficient [2]. PZT with composition close to the morphotropic phase boundary (from Zr/Ti ratio of 40/60 to 65/35) possesses very good ferroelectric properties which is required for fast and reliable memory switching [3]. The PZT has been known to have two crystalline phase, those are the pyrochlore and perovskite. The pyrochlore phase is stable at relatively low temperature and perovskite phase at relatively high temperature. The perovskite phase has cubic, tetragonal, rhombohedral, or orthorhombic structure, depending on the composition and chemical formula of ABO₃. The pyrochlore phase has a cubic fluorite structure and the chemical formula of A₂B₂O₇. Since the pyrochlore phase is centrosymmetric, it does not show ferroelectric properties. In order to use the PZT ceramics in electronic and

electrooptic applications, the PZT ceramics must have a higher perovskite phase content because only the perovskite phase shows the excellent electrical and electrooptical properties that are needed for practical applications [4].

The sol-gel process with precursor system using metal alkoxides is known to lead to highly homogeneous, pure, stoichiometric, low-temperature processing and is also applicable to a wide range of ceramics [5,6]. However metal alkoxides such as Zr and Ti alkoxides fastly hydrolyzed. It is well known that alkoxides of some metals such as Zr, Ti, and Ta react with β -diketones or β -ketoesters form chelate complexes, which are more stable to be hydrolyzed than parent alkoxides [7,8]. These partially stabilized metal alkoxides have recently been recognized as convenient starting materials for the preparation of monolithic gels and homogeneous coating films.

In this study, the preparation of translucent gel-monolith and fine particle gel-derived powder PZT by sol-gel process of partially stabilized metal alkoxides with acetylacetone has been performed.

EXPERIMENTAL

Aparatus

Glass reaction vessel for hydrolysis and condensation reaction., Viscosimeter (Tokyo keisoku kabushiki kaisha), Thermogravimetric-Differential Thermal Analysis (TG-DTA, TAS 100, Rigakku Co), Scanning Electron Microscopy (SEM, JMS-5200, JOEL Ltd), Transmission Electron Microscopy (TEM, JEM-2000 FX II, JOEL Ltd), Energy Dispersive X-ray Spectroscopy (EDX, JEM-2000 FX II, JOEL Ltd), Fourier Transform Infra Red spectroscopy (FTIR, Digilab FTS-65, BIO-RAD), X-ray diffraction (RAD-C system, RPT 300, Rigaku Co), and LCR meter (Ando electric Co, type AG-4301B).

Materials/Reagents

Lead di-i-propoxide ($\text{Pb}(\text{i-C}_3\text{H}_7\text{O})_4$), supplied by Soekawa Chemicals, minimum assay, 99%. Titanium tetra-i-propoxide ($\text{Ti}(\text{i-C}_3\text{H}_7\text{O})_4$), supplied by Soekawa Chemicals, minimum assay, 99%. Zirconium tetra-n-butoxide ($\text{Zr}(\text{n-C}_4\text{H}_9\text{O})_4$), supplied by Soekawa Chemicals. Normal propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$), supplied by

Junsei Chemical minimum assay, 99.5%. Acetylacetone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$), supplied by Kanto Chemical Co. INC., minimum assay, 99.5%.

Experimental procedure

The metal alkoxides, $\text{Pb}(\text{i-C}_3\text{H}_7\text{O})_4$, $\text{Ti}(\text{i-C}_3\text{H}_7\text{O})_4$ and $\text{Zr}(\text{n-C}_4\text{H}_9\text{O})_4$, were dissolved into 1-propanol/acetylacetone solution at room temperature for 4h. The method was similar with reference [9]. The molar ratio of [acetylacetone]/[total metal alkoxides] was 2. The concentration of the total alkoxides was 7.72×10^{-2} mol/l. Twenty times of the theoretically required amount of H_2O was used for hydrolysis. The metal alkoxides solutions were then hydrolyzed at room temperature for 2h by adding 1-propanol/water solution slowly and ensure that the reaction has been completed. As the result, translucent sol was obtained. This sol viscosity was measured by viscosimeter at room temperature. After aging at room temperature for 19 days, translucent monolithic gel was obtained from sol. The gel was dried at 90°C for 18h, and was characterized by TGA-DTA, SEM, TEM, FTIR, and X-ray diffraction. TGA-DTA profiles were measured up to 100°C under O_2 , at a heating rate of $10^\circ\text{C}/\text{min}$. X-ray diffraction measurement was also made for the gel after heating at various temperatures in the range between 300°C and 600°C . FTIR spectra measurements were made for the solutions placed between glass (KRS-5) plates, and for the gel by KBr disk method. The chemical composition of the sample was determined by EDX. The pulverizedgel was pressed at 4 MPa to form disks about 1 cm in diameter, and heated up to 1000°C . The shrinkage and dielectric constant measurements were made at 1 kHz in the temperature range between 25 and 400°C using an LCR meter. Sputtered Au films were used as electrodes. The 2-terminal arrangement was employed, and correction for the stray capacitance was made.

RESULTS

Change of viscosity in the course of gelation.

The viscosity of a mixture of metal alkoxides solution increases as the hydrolysis of alkoxides progress. The change of viscosity with

the reaction time is shown in Fig. 1. It can be seen that the viscosity continues to increase more steadily through the sol to gel conversion process. A slower viscosity increase in the initial

stage and a fast increase of viscosity happened in the final stage. Sol-gel transition and gelation point are 17.75 poise (18 days) and 300 poise (19 days), respectively.

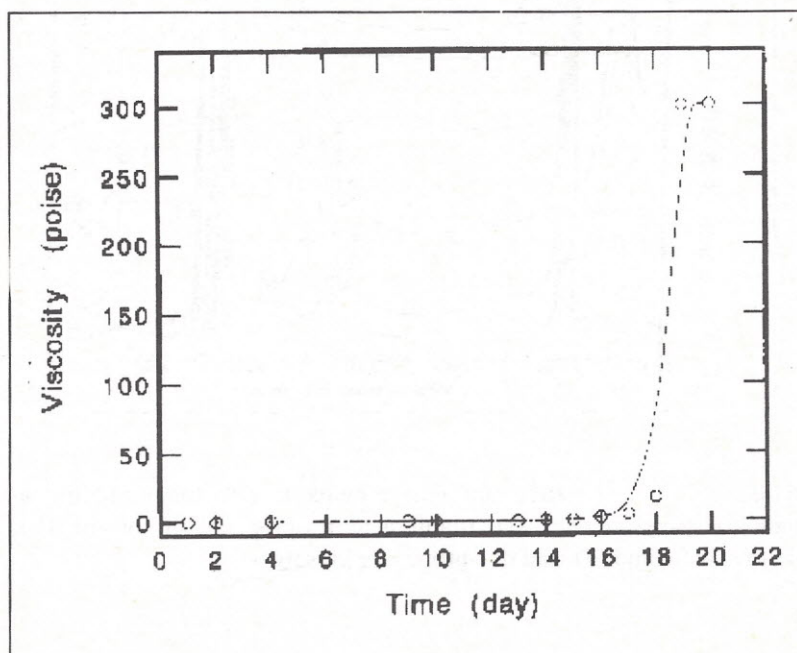


Figure 1. The viscosity change with the reaction time.

Infrared spectroscopy analysis.

In the figure 2 (A), (B), (C), (D), (E) and (F) show the IR absorption spectra of the zirconium tetra-n-butoxide, titanium tetra-i-propoxide, solvent (1-propanol + acetylacetone), titanium tetra-i-propoxide in solvent, zirconium tetra-n-butoxide in solvent and lead di-i-propoxide in solvent, respectively. The loss of the residual organics, formation of chelate and the formation of metal-oxygen bonds can be explained by using FTIR spectroscopy (figure 3). The broad bands around 3500 cm^{-1} may result from free moisture or -OH groups. The band at around $1558\text{-}1341\text{ cm}^{-1}$ indicated the presence of residual organics [10]. The strong band at

around 601 cm^{-1} indicated metal-oxygen band [11].

TGA and DTA analysis.

Figure 4 shows the TG-DTA curves of PZT pulverizedgel after drying at $90\text{ }^{\circ}\text{C}$ for 18h. The TG-DTA curve shows a weight loss of pulverizedgel at about $100\text{ }^{\circ}\text{C}$ followed by endothermic peak due to the evaporation of low-boiling components such as water and alcohol. The sharp exothermic peaks accompanied the weight loss at around $300\text{ }^{\circ}\text{C}$ and near $500\text{ }^{\circ}\text{C}$ were attributed to the combustion of residual organic compounds.

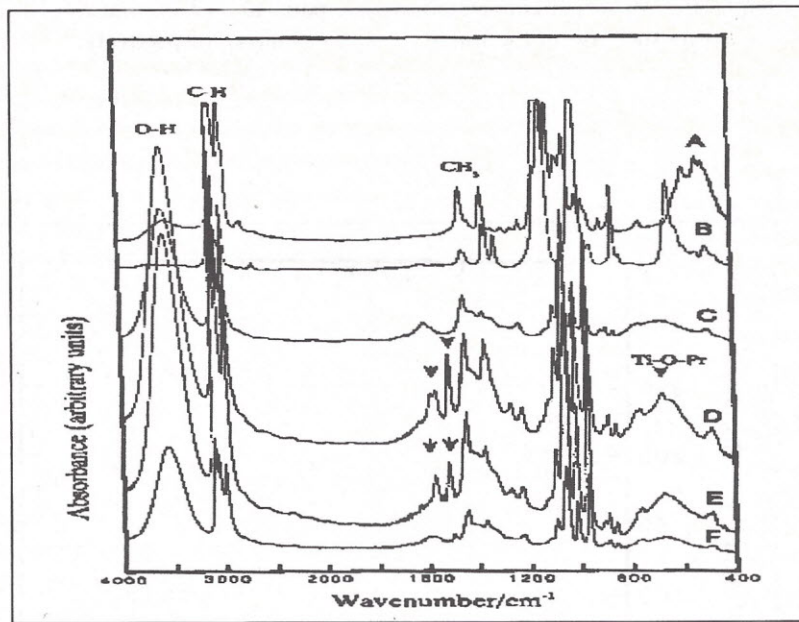


Figure 2. Infrared spectra for : (A) zirconium tetra-n-butoxide, (B) titanium tetra-i-propoxide, (C) solvent (1-propanol + acetylaceton), (D) titanium tetra-i-propanol in solvent, (E) zirconium tetra-n-butoxide in solvent and (F) lead di-i-propoxide in solvent.

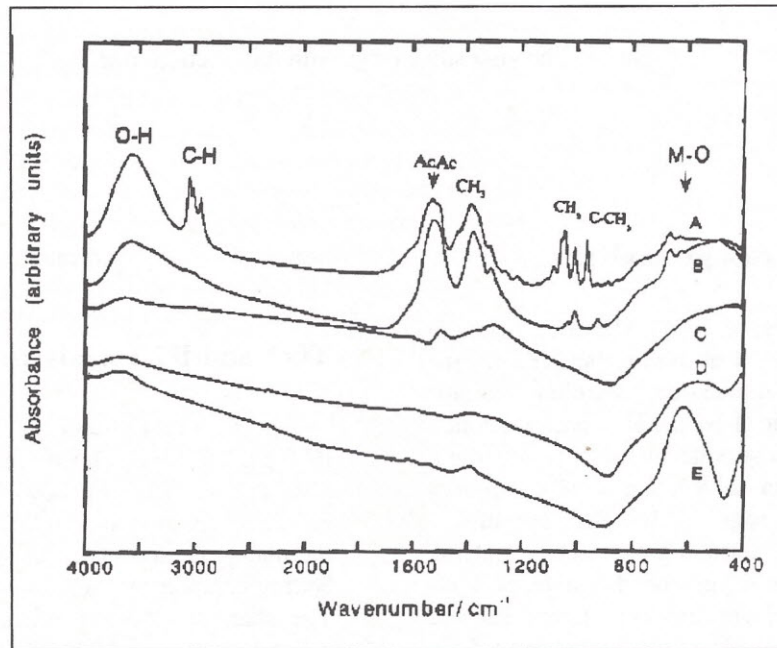


Figure 3. Infrared spectra for the PZT gel: (A) after aging at room temperature, (B) after drying at 90 °C for 18h and after heating for 2h at (C) 300 °C, (D) 500 °C and (E) 600 °C. (M = metal)

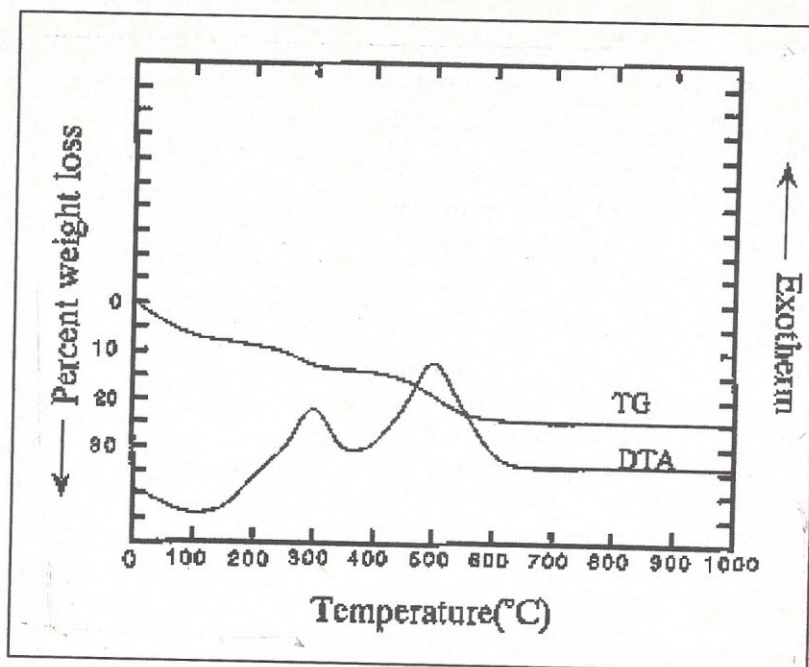


Figure 4. TGA-DTA curves of PZT gel with heating rate 10 °C/min under O₂.

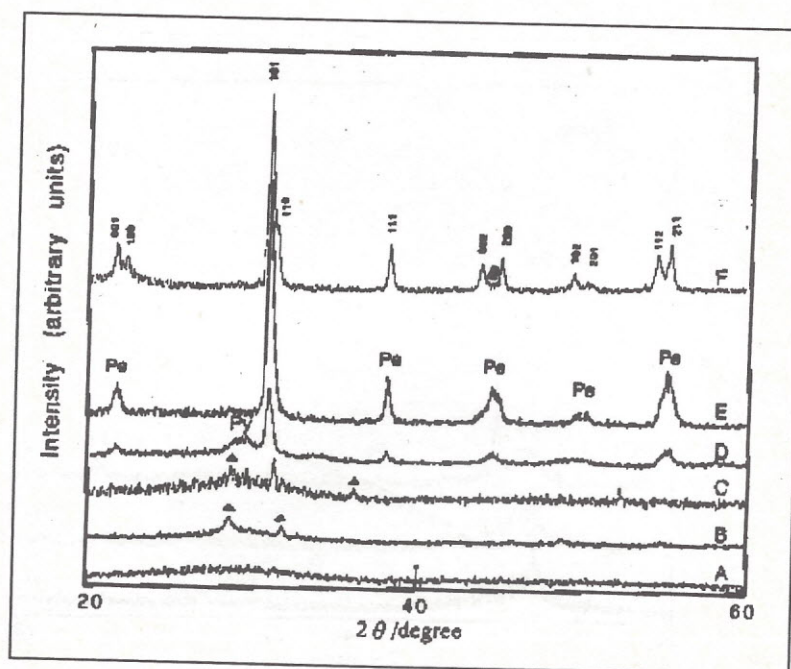


Figure 5. X-ray diffraction patterns for PZT pulverized gel : after drying at 90 °C for 18h, after heating for 2h at 300 °C, 400 °C, 450 °C, 600 °C and after heating at 1000 °C for 30 min. (Pe; Perovskite, Py; Pyrochlore and ; PbO)

X-ray diffraction analysis.

The pulverized gel after drying at 90 °C for 18h, was amorphous by X-ray diffraction (Fig. 5). The diffraction peaks of PbO were found after heating at 300 °C for 2h. After heating at 450 °C for 2 h, diffraction peaks for perovskite PZT (ASTM No. 33-784) and pyrochlore $Pb_2Ti_2O_6$ (ASTM No. 26-142) were observed. The diffraction peaks of pyrochlore phase disappeared after heating at 600 °C and single phase perovskite of PZT was stable up to 1000 °C. The (002) and (001) orientation X-ray peaks can be seen clearly after heating at 1000 °C, where the structure indicated tetragonal phase [12,13]. The diffraction peaks of perovskite and pyrochlore were also found after heating at 430 °C for 24 h (Fig.6).

Dilatometric measurement.

The green density of compacted pulverized gel was approximately 2.9 g/cm³. The green

compact was heated at a heating rate 10 °C/min and hold at various temperatures from 100 to 1000 °C for 30 min. Changes in volume and densities after heating were shown in Fig. 7. After heating up to 300 °C, a large shrinkage of 39% followed by increasing density become 4.2 g/cm³ can be observed. It indicates that content of residual organic was combusted. After heating up to 500 °C, a large shrinkage was observed and followed by increasing density of 55% and 5.3 g/cm³ respectively. This is due to combustion of modifier acetylacetone, dehydration, crystallization and rearrangement. After heating from 500 °C to 800 °C, the densification due to the crystallization was less significant. After heating above 800°C, the shrinkage and densification by sintering were also occurred. The final density (after heating at 1000 °C) of the compacted pulverized gel was 6.9 g/cm³ corresponding to approximately 86 % of the theoretical density [14]. This density is large than that of the compacted powder precipitate (6.1 g/cm³, my previous study) [15].

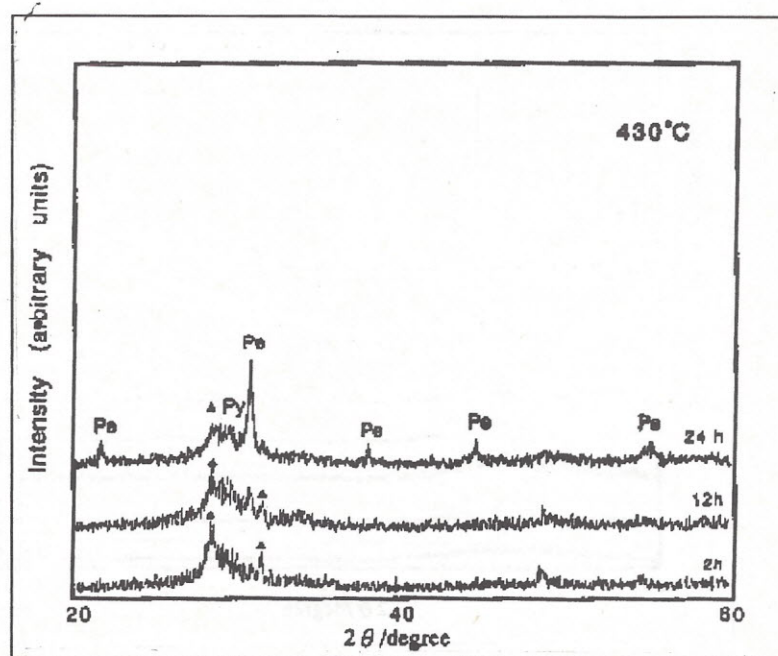


Figure 6. X-ray diffraction patterns for PZT pulverized gel after heating at 40°C for 2h, 12h and 24h.

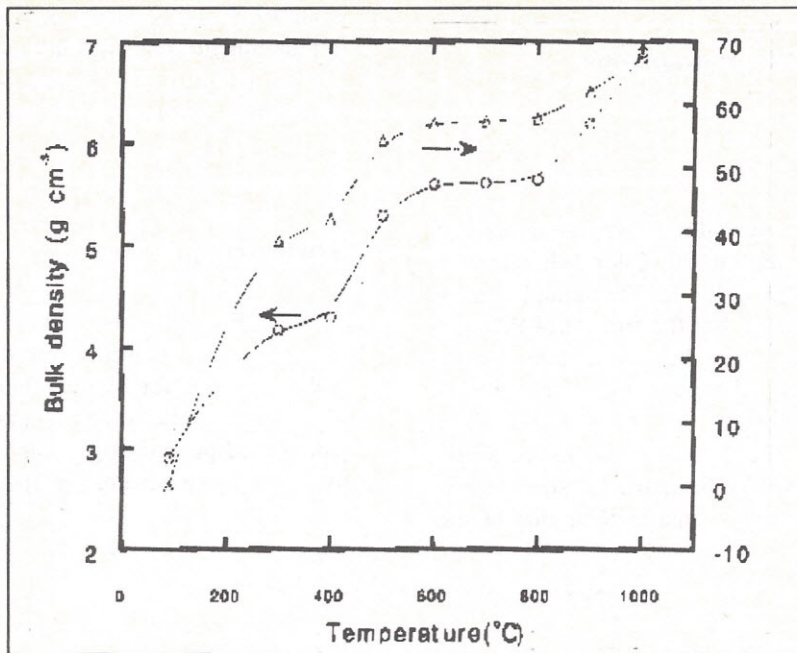


Figure 7. Volumetric shrinkage and density as a function of heating temperature for PZT pulveri-zedgel.

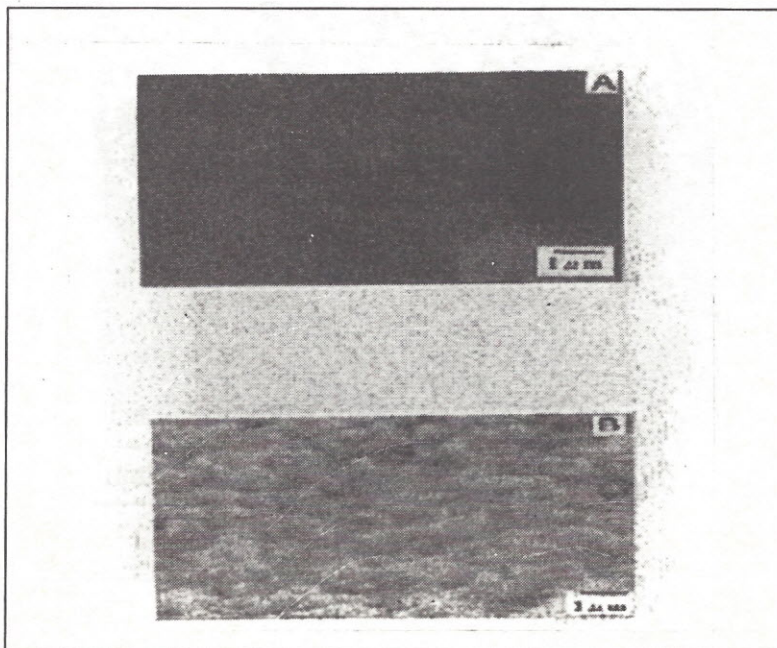


Figure 8. SEM photographs of PZT gel: after drying at (A) 90°C for 18h and after heating at (B) 600°C for 2h.

SEM and TEM photographs.

Figure 8 shows the SEM photographs of the gel after drying at 90 °C for 18h. and also after heating at 600 °C for 2h. The samples after being dried indicated that the surface of PZT gel was very smooth. After heating at 600 °C, the form of PZT gel changed from smooth to agglomerates. Figure 9 shows a TEM photograph of the gel at room temperature. This photo shows that the particle size of gel, 2-5 nm in diameter, is smaller than that of the

powder precipitate, 5-10 nm in diameter [15]. Compositional analysis by EDX was carried out on pulverized gel heated previously at 600 °C for 2h (Fig.10). The results was 49.29 : 27.80 : 22.91 ratio (atomic %) of Pb : Ti : Zr.

Dielectric properties.

Figure 11 shows the temperature dependence of the dielectric constant of the sintered gel at 1000 °C for 30 min. This results indicates that the dielectric constants value of compacted pulverized gel was higher than that of compacted powder precipitate [15].



Figure 9. TEM photograph of PZT gel after aging at room temperature for several days.

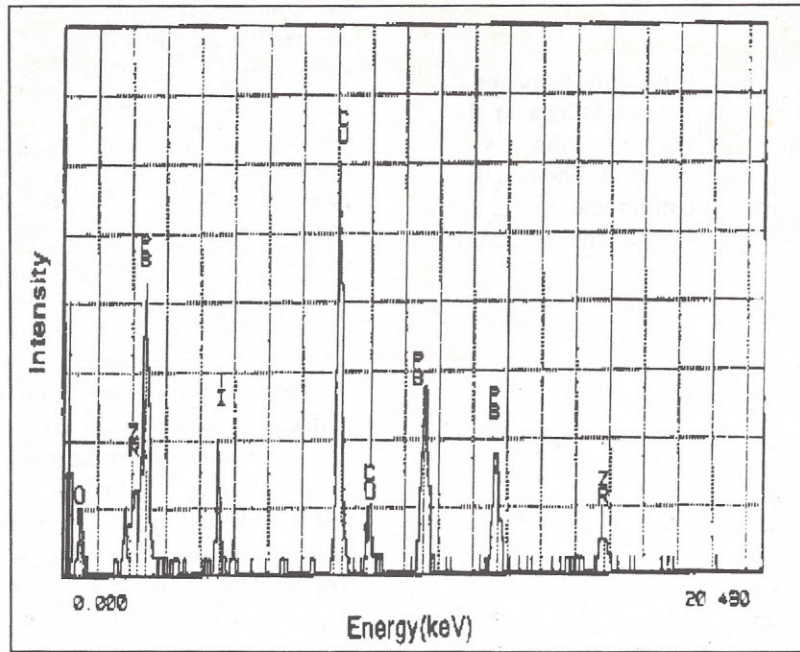


Figure 10. EDX spectra of PZT pulverized gel after heating at 600 °C for 2h

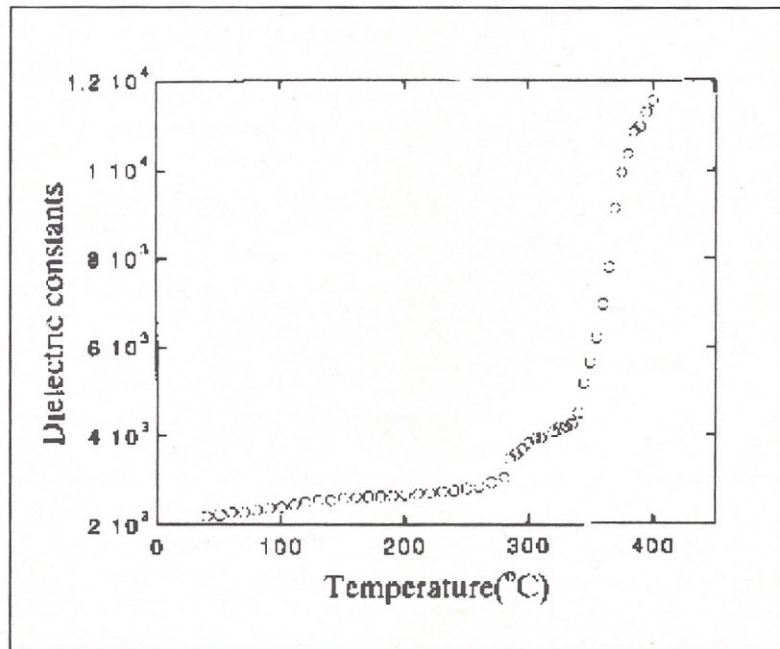
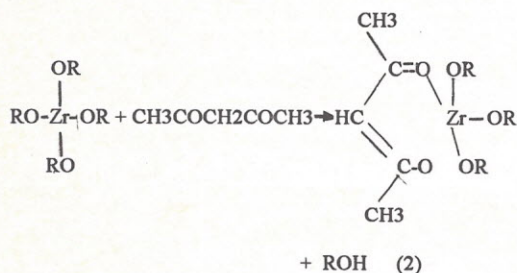
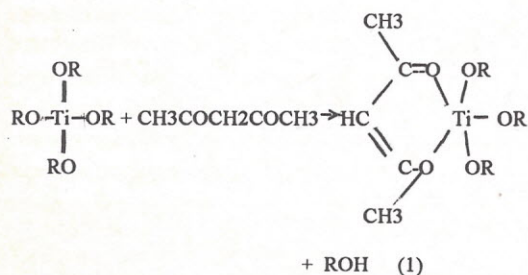


Figure 11. Temperature dependence of dielectric constant at 1 kHz for compacted pulverized gel after heating at 1000°C for 30 min.

DISCUSSION

To avoid the occurrence of a precipitation, acetylacetone (acacH) was added to the mixed solution of metal alkoxides as a modifying agent before adding H₂O. The reaction of acetyl-acetone with titanium and zirconium alkoxides may be expressed by the following simplified equation :



The corresponding IR spectrum has a broad absorption band near 637 cm⁻¹ assigned to ν (Ti-O-Pri) and bands at 1603 and 1528 cm⁻¹ (Fig.2 D, arrows) assigned to acac groups bonded to Ti. This result is similar with reference [10]. A pair of absorption peaks are observable at 1589 and 1532 cm⁻¹ (Fig.2 E, arrows) assigned to acac groups bonded to Zr. This result is similar with reference [8]. In Fig. 2F, showed the solution part of the lead di-*i*-propoxide in *i*-propanol/acetyl-acetone solution in which precipitate was occurred. The precipitate indicates that lead di-*i*-propoxide is difficult to become chelate form. These modified alkoxides, zirconium tributoxide mono acetylacetonate and titanium tri-propoxide mono acetylacetonate are assumed to react with unchelated lead alkoxide and then hydrolyzed /poly-merized to form gel. In the figure 3A and B, the gel at room temperature and after aging at 90 °C for 18h, the most significant feature is the presence of a broad band at around 1554 cm⁻¹ which can be assigned to be ν (C-O) and ν (C-C) vibrations of acetylacetonate group bound to the metal cation. This indicates the chelation of Zr and Ti

by the acetylacetonate groups. The band occurred at around 1403 cm⁻¹ due to presence of methyl group [16]. These peaks become weak after heating at 300 °C for 2h and finally disappear after heating at 500 °C, indicating that the acetylacetone group can be eliminated by heat treatment at around 500 °C; thermal analysis of the pulverizedgel (Fig. 4) also shows that the residual organic was burned out at around 500 °C. After heating at 600 °C for 2h, the absorption peaks in figure 3 shows a very strong metal-oxygen bands at 601 cm⁻¹ and this absorption peak is very similar to that of lead titanate and lead zirconate [11].

The sharp exothermic peak accompanied the weight loss near 500°C (Fig.4), showed that the residual organic compound was combusted and crystallization was occurred. The higher temperature is needed for combustion of the residual organic compound which was used on modified metal alkoxides than unchelated organic compounds. That is due to the chelating ligand of acetyl-acetonate complexes has stronger bonding than free residual organic compounds.

XRD data for dried at 90 °C for 18h is amorphous and after heating at 300 °C for 2h, the diffraction peaks of PbO were found (Fig. 5). It indicates that Zr and Ti alkoxides which were modified with acacH become chelate complexes form. Finally the modified alkoxides is lower to be hydrolysis than unchelated Pb alkoxide. As result the crystalline PbO therefore, could be formed easier. The perovskite PZT phase and py-rochlore Pb₂Ti₂O₆ phase were occurred after heating at 450 °C for 2h or at 430 °C 24 h. In these heating temperatures the pyrochlore phase transforms into the perovskite PZT phase via the following formal equation : Pb₂Ti₂O₆ + 2ZrO₂ + 2PbO → 4Pb(Zr,Ti)O₃. After heating at 600 °C only single phase perovskite PZT was detected. After heating at 1000°C for 30 min. the tetra-gonal perovskite PZT fixes stable and has high dielectric constant and the density is 6.9 g/cm³.

At temperature higher than 800°C, shrinkage by sintering was observed. The higher bulk density of the compacted pulverizedgel may be attributed to the small particle size, observed by TEM, and resulted in the higher dielectric constant of the sintered compact gel.

CONCLUSIONS

Translucent monolithic PZT gel with 31 median diameter of about 2-5 nm can be prepared by controlling polymerized condensation of titanium and zirconium alkoxides which stabilized by chelation with acetyl-acetone. In the infrared spectra for gel at room temperature and after aging at 90 °C for 18h, the most significant peaks are the presence of broad band at around 1554 cm^{-1} which can be assigned to the ν (C-O) and ν (C-C) vibrations of acetylacetanate group bound to the metal cation. This pulverized-gel was amorphous by X-ray diffraction. The crystallization start at 300 °C with the formation of PbO. After heating at 400 °C for 2 h, diffraction peaks of PbO and pyrochlore were observed. They are transformed to the perovskite phase at 450 °C. The diffraction peaks of perovskite and pyrochlore phase were also found after heating at 430°C for 24 h. The heated compact pulverizedgel has higher bulk density than the heated compact powder [15], because of its smaller particle size, resulting in the higher dielectric constant.

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