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FT-IR Spectroscopic Study of Preparation of Lead Zirconium Titanate (PZT) by Sol-Gel Processing

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Gelation time, gel structure and volatility of by-products during gelation of PZT sol-gel processing were investigated by FT-IR spectroscopy. FT-IR spectroscopic study was performed on PZT gels with the various H_2O contents (1, 2 and 3 mol) and the several types (HNO_3, NH_4OH) and amounts (0.1, 0.2 mol) of catalysts, monitoring temporal (0, 1, 3, 10 weeks, 3 months and 3 years) and thermal (100-700 °C) changes of FT-IR spectra. The interpretation of temporal change of the spectra revealed two trends. One is under the condition of 1 mol H_2O, 1 mol H_2O+0.1 mol HNO_3, 3 mol H_2O and the other is for 1 mol H_2O+0.1 mol NH_4OH, 2 mol H_2O, 1 mol H_2O+0.2 mol HNO_3. The gel structures and the gelation times for these conditions were discussed in comparison with the reported results of SiO_2, and we suggested the reaction mechanisms for these structural characteristics. Thermal variation of FT-IR spectra was interpreted as the evolution processes of gel by investigating the evaporation of solvent and the decomposition of organic residues.

Introduction

An increasing attention has been focused in last few years on ferroelectric thin films for the potential applications of electronic and electro-optic devices, which can be used as pyroelectric sensors,[1] non-volatile memories,[2] substrate materials for surface acoustic wave (SAW) elements,[3] decoupling capacitors[4] and ferroelectric gate field-effect-transistors (FETS).[5] These devices employ ferroelectric thin films such as $Pb(Zr,Ti)O_3$, $(Pb,La)(Zr,Ti)O_3$, $PbTiO_3$, $BaTiO_3$, $KNbO_3$, $(Sr,Ba)Nb_2O_6$, $(Pb,Ba)Nb_2O_6$.[6-8] In the present study, the gelation process of PZT, prepared by a sol-gel processing for the thin films, was investigated with the FT-IR spectra of PZT gels under various different conditions. That is, the evaporation of solvent and/or by-products, and the structure and gelation time of PZT gel were studied. The composition of PZT was chosen to be $Pb(Zr_{0.52}Ti_{0.48})O_3$, the morphotropic boundary (MPB) of rhombohedral and tetragonal structure. It is well known that PZT shows optimized dielectric properties at this composition by the dielectric constant, polarization, piezoelectricity and SAW propagation.[9,10]

PZT thin films have been fabricated using highly equipment-dependent vacuum deposition technique, such as RF sputtering,[11,12] ion beam deposition,[13] electron beam evaporation,[14] but these techniques are very costly and hard to obtain the stoichiometric composition of PZT thin films. Sol-gel processing, on the contrary, provides remarkable advantages such as low-cost, high purity, high homogeneity, low temperature synthesis and versatile formation of various shapes. Sol-gel processing is a chemical method based on inorganic polymerization of appropriate precursors in organic or inorganic solvent.[15] Thin film of PZT can be fabricated by coating a stock solution on substrates using spin coater or dip coater, and by subsequent pyrolysis to promote polymerization, to remove solvent and to decompose organic residues, and by final heat treatment to form desired perovskite structure.

The properties of sol-gel derived PZT powders or thin films are closely related to the structure of gel, while gel structure depends on the amount of H_2O and the catalyst (type, amount) used in gelation process.[16-18] Therefore, we studied in this paper the progress of PZT gelation with various H_2O contents (1, 2 and 3 mol) and the several types (HNO_3, NH_4OH) and amounts (0.1, 0.2 mol) of catalysts, by monitoring temporal (0, 1, 3, 10 weeks, 3 months, 3 years) and thermal (100-700 °C) changes of FT-IR spectra. The structure of polymer and the evaporation of solvent and/or by-products and the gelation time were discussed with peak positions and shifts of the FT-IR spectra.

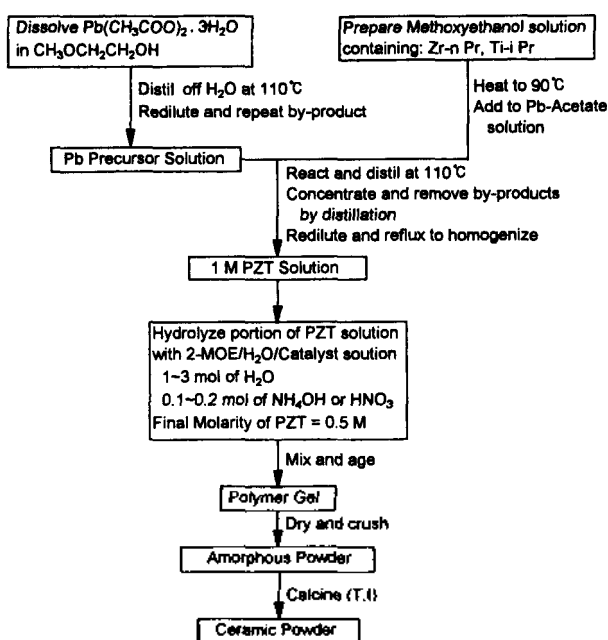*Authors to whom correspondence should be addressed.

FT-IR Study of Lead Zirconium Titanate by Sol-Gel Processing

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Figure 1. Flow diagram for the preparation of PZT solution and powder.

Figure 2. FT-IR spectrum of Lead Acetate Trihydrate, $(Pb(Ac)_2 \cdot 3H_2O)$.

Experimental

Stock solution of PZT was prepared using complex alkoxide method. The procedure for stock solution preparation is schematically shown in Figure 1.

2-Methoxyethanol $(CH_3OCH_2CH_2OH$, Aldrich) was used as a solvent and lead acetate trihydrate $(Pb(Ac)_2 \cdot 3H_2O$, Alfa), zirconium n-propoxide $(Zr(OC_3H_7)_4$, 70% in propanol, Alfa) and titanium isopropoxide $(Ti(OC_3H_7)_4$, Aldrich) were used as well.[19-21] All stock solutions were prepared under dry N_2 or vacuum conditions using Schlenk apparatus. Pb precursor was prepared through two additional dilution and distillation to complete the dehydration. The Pb precursor solution was concentrated to 1 M during the final step and was ready for combination with Zr-Ti precursor solution. Two stock solutions, Pb and Zr-Ti, were mixed at room temperature and reacted at 110 °C. Three successive dilutions with 2-Methoxyethanol (2-MOE) and vacuum distillation were used to remove the by-products which was mainly methoxyethyl acetate $(CH_3COOCH_2CH_2CH_2OCH_3)$, creating stable solution.[22] The volume of the final solution was then adjusted to give 1 M PZT stock solution.

Bulk gel was prepared by mixing 1 M PZT stock solution and equi-volume of 2-Methoxyethanol hydrolysis solution, which was made of 2-MOE with the addition of H_2O and 0.1-0.2 mol of catalysts $(NH_4OH$ or $HNO_3)$. As a result, a transparent PZT bulk gel was obtained with 1-3 mol of H_2O added. The FT-IR spectra of the gels were measured by FT-IR spectrometer (Mattson) at room temperature, and the attention was particularly focused on the synthesis step of complex alkoxide solution and the gelation step, after the addition of H_2O and catalyst, and the crystallization step of gel by heat treatment as shown in Figure 1. Samples used for temporal change of FT-IR spectra were preserved in closed vial under ambient atmosphere at room temperature.
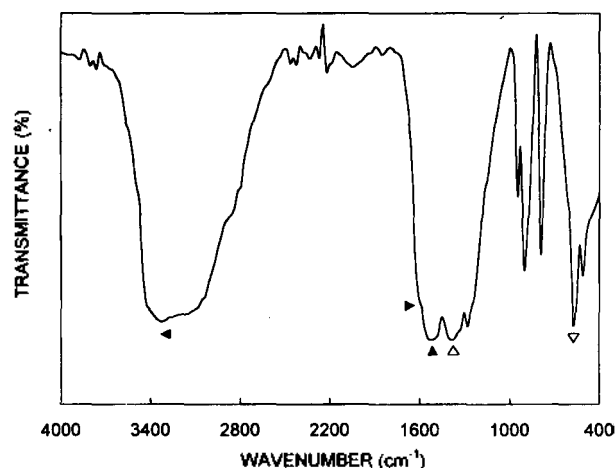
Results and Discussion

FT-IR spectrum assignments of the starting materials

Lead acetate trihydrate $(CH_3COO\text{-}Pb\text{-}OOCCH_3 \cdot 3H_2O)$. The important peaks in Figure 2 are those of CH_3COO radical. The CH_3COO radical of the sample forms an ionic bond with Pb^{2+}, which means that the CH_3COO radical possesses both characteristics of CH_3COO^- and CH_3COOH. In details, the broad band (◄) at 3600-2800 cm⁻¹ represents superimposed peaks of the stretching mode of OH, hydrogenically bound in CH_3COOH and H_2O and the stretching mode of CH in alkyl group (3000-2850 cm⁻¹). Peaks at 1560 cm⁻¹ and 1412 cm⁻¹ are attributed to asymmetric (▲) and symmetric stretching (△) of COO^- in CH_3COO.[23] The asymmetric stretching peak of COO^- at 1560 cm⁻¹ is overlapped with the bending peak of H_2O (1595 cm⁻¹) (►). The symmetric stretching peak of COO^- at 1412 cm⁻¹ is also overlapped with the bending peaks of CH_3 (1450 cm⁻¹, 1375 cm⁻¹). The stretching peak (▽) of Pb-O can be observed at 650 cm⁻¹.[23,24]

Titanium isopropoxide: Ti(OR)₄. C-O stretching peak (▷) at 1128 cm⁻¹, Ti-OR stretching peak (▽) at 616 cm⁻¹ and H_2O bending peak (►) near 1600 cm⁻¹ are the important peaks in Figure 3. Since the sample contains H_2O, the gelation is expected to progress to some extent through hydrolysis of metal alkoxide during the formation of Zr-Ti precursor.

Zirconium n-propoxide: Zr(OR)₄. Most peaks correspond to propanol solvent, and Zr-OR stretching peak (▽) near 625 cm⁻¹ is shown in Figure 4.

PZT stock solution

FT-IR spectral peaks in Figure 5 can be attributed to various substances (sample, solvent, by-products), which hazzles an interpretation of their characteristics. However, C=O stretching mode at 1741 cm⁻¹ (◁) and COO^- asymmetric stretching mode at 1575 cm⁻¹ (▲) are found only in by-product (Methoxyethyl acetate) and CH_3COO-Pb, thus, these peaks can confirm a presence of ester or CH_3COO radical in PZT stock solution. In addition, it is worthy to note that a M-OR stretching peak (▽), which should be observed be-
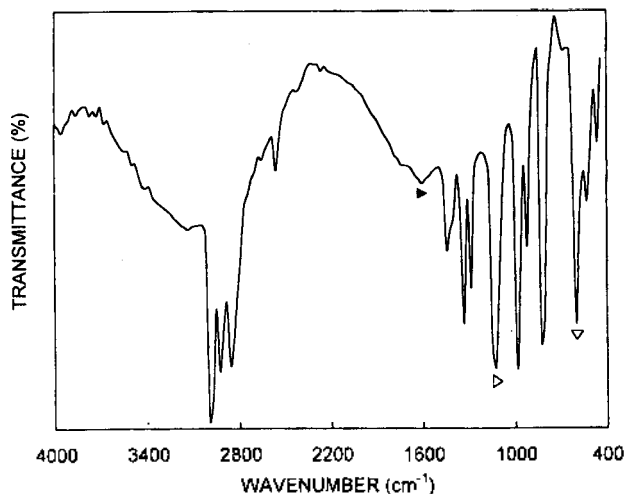
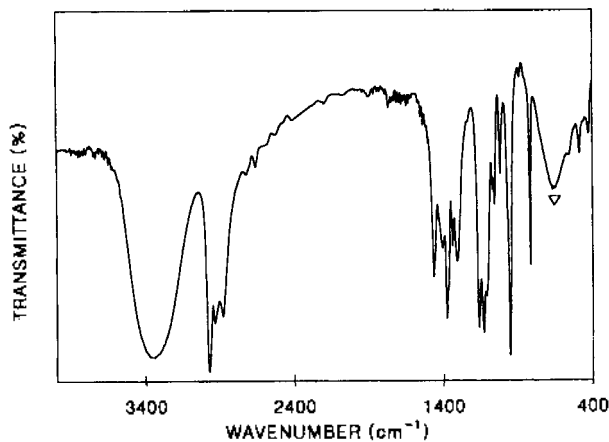**Figure 3.** FT-IR spectrum of Titanium isoproxide, (Ti(OR)₄).

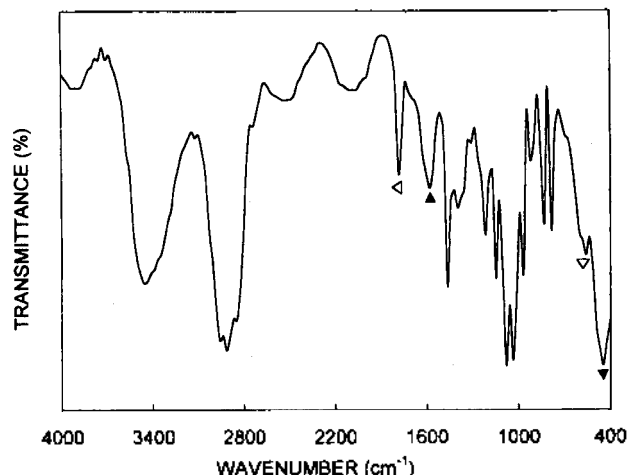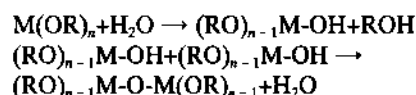**Figure 4.** FT-IR spectrum of Zirconium *n*-propoxide, (Zr(OR)₄).

Figure 5. FT-IR spectrum of PZT stock solution.

fore the formation of metal-oxygen bond, was appeared near 650 cm⁻¹. One unusual feature in the spectra is the observation of strong peak (▼) near 410 cm⁻¹ which has not been found in the spectra of the other samples (Figure 2-Figure 4). It might be attributable to metal-oxygen stretching peak of M-O-M bond which should be unique in PZT stock

solution.[23,25] This can be further interpreted that the metal-oxygen bond strength of M-O-M is weaker than that of M-OR. In addition, the presence of M-O-M peak can verify a gelation during the formation step of Zr-Ti precursor.

The followings are the fundamental chemical reactions of sol-gel processing and the listed chemical formulas of the possible by-products from complex alkoxide solution synthesis process of PZT.

Hydrolysis of metal alkoxide and condensation with 1 mol H_2O; stock solution synthesis step

$$M(OR)_n + H_2O \rightarrow (RO)_{n-1}M\text{-}OH + ROH$$
$$(RO)_{n-1}M\text{-}OH + (RO)_{n-1}M\text{-}OH \rightarrow$$
$$(RO)_{n-1}M\text{-}O\text{-}M(OR)_{n-1} + H_2O$$

Further hydrolysis and condensation with *n* mol H_2O and catalysts; gelation step

$$M(OR)_n + nH_2O \xrightarrow{\text{H}^+ \text{ or OH}^-} M(OH)_n + nROH$$
$$M(OH)_n \longrightarrow MO_{n/2} + \frac{n}{2}H_2O$$
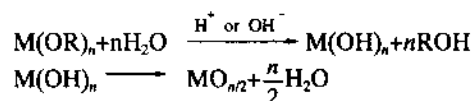
Major by-products of PZT gelation: $CH_3COOCH_2CH_2CH_2$ OCH_3, $CH_3CH_2CH_2OH$, $(CH_3)_2CHOH$, H_2O.

Temporal change of FT-IR spectra with various conditions

Temporal change (0, 1, 3, 10 weeks, 3 months, 3 years) of FT-IR spectra during polymerization, as functions of ca-
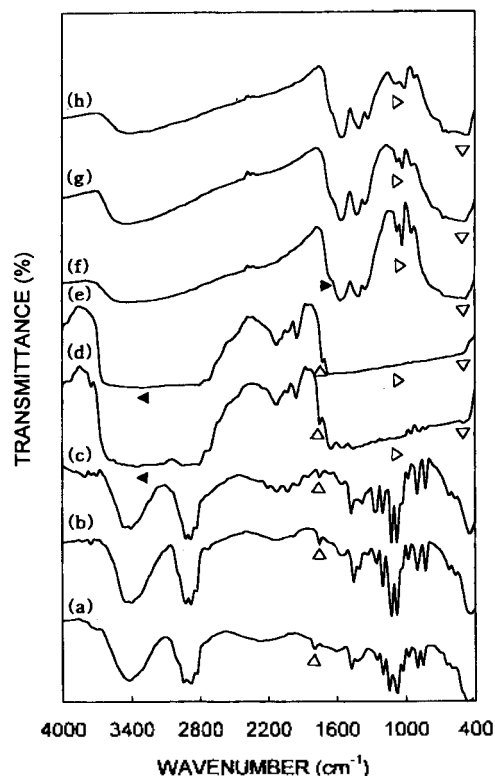

Figure 6. [Trend A] FT-IR spectra of the gel with 1 mol H_2O as a function of aging time: (a) as-prepared, (b) 1 week, (c) 3 weeks, (d) 10 weeks, (e) 3 months, (f) 3 years, and (g) the gel with 1 mol $H_2O+0.1$ mol HNO_3 after aged for 3 years, and (h) the gel with 3 mol H_2O after aged for 3 years.
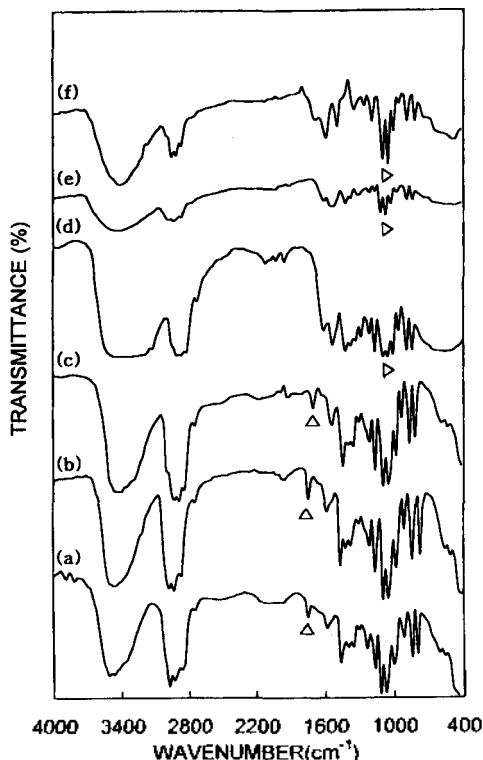
Figure 7. [Trend B] FT-IR spectra of the gel with 1 mol H_2O+ 0.1 mol NH_4OH as a function of aging time: (a) as-prepared (b) 1 week (c) 3 weeks (d) 3 years, and (e) the gel with 2 mol H_2O after aged for 3 years, and (f) the gel with 1 mol H_2O+0.2 mol HNO_3 after aged for 3 years.
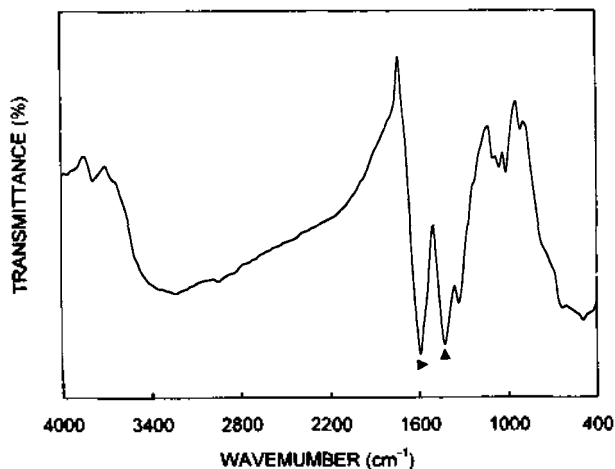

Figure 8. FT-IR spectrum of powdered PZT gel after heating at 100 °C for 2 hours.

talyst and amount of H_2O, manifests two trends as shown in Figure 6 and 7.

Trend A (Figure 6) shows the spectra of gelation with 1 mol H_2O, 1 mol H_2O+0.1 mol HNO_3, 3 mol H_2O, respectively. Trend B (Figure 7) shows those with 1 mol H_2O+0.1 mol NH_4OH, 2 mol H_2O, 1 mol H_2O+0.2 mol HNO_3. In Figure 6, the spectra of the sample aged for 3 months were shown only for the sample with 1mol H_2O since the other samples exhibited almost same trend. Likewise, in Figure 7, the spectra of the sample aged for 3 weeks were limited to
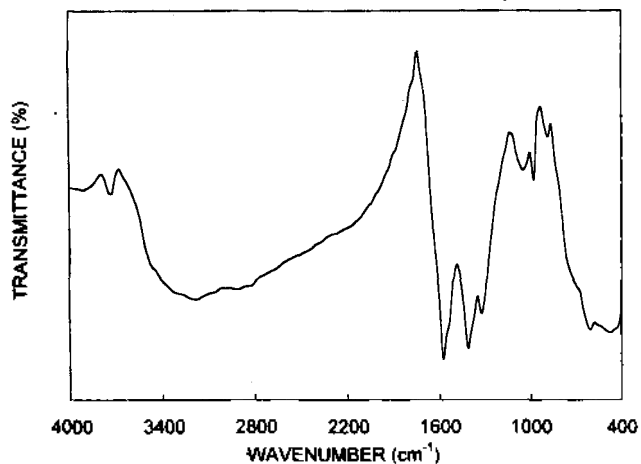

Figure 9. FT-IR spectrum of the gel with 2 mol H_2O+0.2 mol NH_4OH after aged for 3 months.

the sample with 1 mol H_2O+0.1 mol NH_4OH. In trend A, no significant change of spectra was observed up to 3 weeks. However, those for 10 weeks (Figure 6(d)) showed strong H_2O (◄) and ester (△) peaks, while only weak C-O stretching peaks (▷) for solvent or alcohols and none of M-O-M peaks (▽) were observed. It implies that OH stretching peak at 3400 cm^{-1} can be detected after 10 weeks since they can reside both in by-products (alcohols, ester, H_2O) or solvent and in hydrogen bonded H_2O inside the gel, while C-O stretching was attenuated upon the evaporation of alcohols or solvent after 10 weeks and M-O-M peaks seem to be overwhelmed by the peaks of by-products (ester, H_2O). This interpretation is supported by the fact that M-O-M peaks become visible in the sample aged for 3 years. The C =O stretching peaks of by-product ester, which were prominent in the samples aged for 10 weeks, were disappeared after 3 years in Figure 6(f, g, h). The spectra after 3 years (Figure 6(f, g, h)) in trend A were further interpreted as follows. The broad peaks in 3700-2400 cm^{-1} were attributed to a superposition of hydrogen bonded OH stretching peak in CH_3COOH and hydrogen bonded OH stretching peak in H_2O. The peaks in 1550 cm^{-1} and 1440 cm^{-1} should be recognized as a stretching peak of COO$^-$ in CH_3COO-Pb.

Trend A conclusively implies that, even though alkoxy radicals bound to polymer gel were almost decomposed and the solvent or by-products were evaporized, CH_3COO and OH still resided in gel and H_2O was present in the gel as the form of hydrogen bonding (the presence of H_2O can be verified by the H_2O bending peaks (▶) near 1600 cm^{-1}). Furthermore, these temporal changes are well compatible with the thermal change of the gel (Figure 8). It is well known that gelation can be promoted at higher temperature.[2b] Thus, the comparison of temporal change and thermal change of the spectra evidenced that the gelation was completed in trend A. The approximated gel structure of trend A is as follows (the hydrogen bonded H_2O is not represented in the structure).
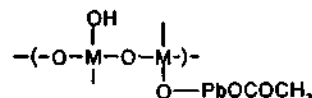
Figure 8 shows that the peaks from CH_3COO-Pb (▲) were detected even though the gelation was completed in PZT system, which provides the information on the structure of gel upon gelation. That is, when the starting material; CH_3COO-Pb-$OOCCH_3$ was developed to the gel through hydrolysis reaction, Pb is present in the form of bridging type; -M-O-M(O-Pb-$OCOCH_3$)O- rather than back-boning type; -M-O-Pb-O-M- in gel as shown in the above gel structure.[23]

Figure 9 shows the spectrum of sample with 2 mol H_2O+ 0.2 mol NH_4OH after polymerization for 3 months. It indicates that 0.2 mol NH_4OH is more effective catalyst for gelation than the other catalysts.

In trend B (Figure 7), the temporal change of FT-IR spectra from 1 week to 3 years was minimal except for the amplitudes of the peaks of as-prepared gel, which implies that the alkoxy radicals (▷) remain in gel even after 3 years. However, the C=O stretching peak (△) of ester was not appeared in Figure 7(d, e, f). This results indicate that even though by-products such as ester and alcohols were evaporized after 3 years in trend B, the alkoxy radicals are still remained in gel. Thus it was recognized that the gelation was not completed even after 3 years in trend B. The approximated gel structure of trend B is as follows.

$$-(-O-\underset{|}{\overset{\overset{\displaystyle OR}{|}}{M}}-O-\underset{\underset{\displaystyle O-PbO COCH_3}{|}}{M}-)-$$
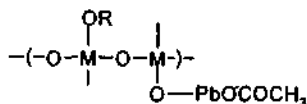
The temporal changes in trend A and trend B can be interpreted in comparison with the results of sol-gel derived SiO_2. The characteristics of sol-gel processing of SiO_2 as functions of H_2O contents and catalysts were reported as follows[27]: (1) With small amount of water and acidic catalyst, gel has a linear structure and the rate of gelation was faster than when basic catalyst in the same amount was used. (2) With small amount of water and basic catalyst, gel has colloidal particles and the rate of gelation was relatively slower. (3) With excessive amount of water, gel has the same characteristics as basic catalyst used, resulting in colloidal particles stfucuture, however, the rate of gelation in this case is fast since aggregated colloidal particles are formed. With these backgrounds, our experimental data can be interpreted as follows. For trend A, the gel with 1mol H_2O+ 0.1 mol HNO_3 has a linear structure, while the gel with 3 mol H_2O has aggregated colloidal particles structure with faster gelation rate. In trend B, the gel with 1 mol H_2O+0.1 mol NH_4OH has a colloidal particles structure with a relatively longer gelation time than the corresponding situation in trend A. The gel with 1 mol H_2O has a similar characteristic to that with 1 mol H_2O+0.1 mol HNO_3, while the gel with 2 mol H_2O in trend B is similar to that with 1 mol H_2O+0.1 mol NH_4OH. It is worthy to note that the gel with 1 mol H_2O+0.2 mol HNO_3, *i.e.* a small amount of water and excessive acid catalyst, exhibits slower gelation rate.

These structural characteristics of gel seem to be due to the reactivity of functional groups (-OR, -OH) of metal alkoxide or hydroxide in various conditions. As a plausible reaction mechanism, we suggest the following reaction dynamics of the gelation processes in various conditions. Firstly, the gelation process of PZT with small water content (1

mol H_2O) would be progressed by the partial hydrolysis of metal alkoxide because of small water content used in the reaction. That is, alkoxide functional groups (-OR) could be remained in the metal hydroxide after the hydrolysis of metal alkoxide. The polymerization or gelation of PZT would be progressed with these partially hydrolyzed metal alkoxides, and then the unreacted alkoxide functional groups which remained in the polymerized PZT gel could be hydrolyzed by H_2O molecules produced through the condensation reactions of metal (partial) hydroxides. Thus, the spatial direction of polymerization in the gel could be united and the gel structure in this condition became linear. The structure of this gel could be sketched as follows.
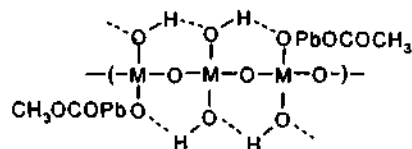
Secondly, the gelation process of PZT with the excessive water contents (2 or 3 mol H_2O) would be progressed by more hydrolysis of metal alkoxide than that in case of small water contents. Thus the polymerization or gelation of metal alkoxides could be progressed in all directions to form metal oxygen bondings. Therefore, the gel structure in this condition become colloidal particles as follows.
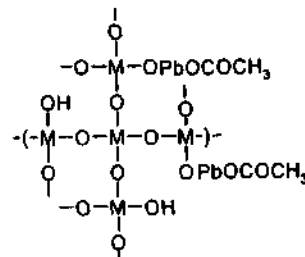
Thirdly, the gelation process with basic or acidic conditions could be considered as follows. It should be reminded that the basic solution has an anionic characteristic of OH^-, and the acidic solution has a cationic characteristic of H_3O^+ in aqueous solution. Thus, in the basic aqueous solution, the electrostatic attractive force between OH^- produced by condensation reaction of metal (partial) hydroxides and its nearest metal cation in metal alkoxide could be possible. That is to say, H_2O molecule produced by the condensation reaction of metal (partial) hydroxides would be exist in the form of OH in base catalytic solution, and this OH^- species couldn't be completely separated from the metal cation of the metal alkoxide dimer, produced by the condensation reaction, because of the electrostatic attractive force between this OH^- species and its nearest metal cation. Thus, this OH^- species would substitute for the different alkoxide functional group of the metal alkoxide dimer; the condensation product. Therefore, the direction of polymerization in the molecule would be random as in the excessive water used in the reaction. So, the gel structure in this condition would be colloidal particles. On the other hand, when the gelation process is progressed with the acidic catalysts, the H_2O produced by the con-

densation reaction of the metal (partial) hydroxides would be exist in the form of H_3O^+ in acidic aqueous solution. Thus the repulsive force between H_3O^+ and its nearest metal cation of the metal alkoxide dimer; the condensation product would be possible. Therefore, the H_3O^+ produced by the condensation reaction would be diffused to the neighboring other metal alkoxides, resulting in the hydrolysis of other metal alkoxide and the linearity of gel as in the small water contents used in the reaction.

Thermal evolution of FT-IR spectra

FT-IR spectra of the PZT gel prepared from stock solution with the various catalysts are shown in figure 10 as a function of heat treatment temperature.

In Figure 10, the gel with 2 mol H_2O+0.2 mol HNO_3 is apparently shown for a general interpretation, since the other gels displayed a similar trend. The spectra of the gel heated at 100 °C shown in Figure 10(a) was almost identical to that aged for 3 years in trend A as in the previous discussion. And the attenuation of CH_3COO-Pb peaks (OH stretching of CH_3COOH (◀) and COO^- stretching peak (▲)) by an heat treatment was observed in Figure 10. However, the metal oxygen stretching peak (▼) of M-O-M bond was still observed. It is worthy to note that the M-O-M peak is shifted to higher frequency by a heat treatment up to 550 °C. This can be interpreted that the metal-oxygen bond became stronger as the gel evolved to a perovskite structure.[23] Based on these results, it can be inferred that, by a heat treatment at about 100-250 °C, the alkoxy radicals bound to

gel were desorbed and by-products (ester, alcohols) or solvent were evaporated along with the formation of pyrochlore structure.[28,29] Furthermore, the heat treatment over 400 °C removed almost all peaks from CH_3CHOO-Pb. It has been reported for PZT gels that pyrochlore structure was dominant if the gel was heated at ~400 °C, while perovskite structure was dominant if it was heated at ~550 °C.[30,31]

Conclusion

The following results were obtained from the FT-IR spectroscopic study on sol-gel processing of PZT. The progress of polymerization could be understood from the spectra of raw materials and PZT stock solutions. Upon examining the gelation step of the solution as functions of the amount of water and the type of catalyst, the gel with 1 mol H_2O, 1 mol H_2O+0.1 mol HNO_3, 3 mol H_2O showed a faster gelation rate than those with 2 mol H_2O, 1 mol H_2O+0.1 mol NH_4OH, 1 mol H_2O+0.2 mol HNO_3. These phenomena seem to be ground on the structure of gel and further suggest that the structure of gel and the gelation rate are sensitive to the amount of water and the type of catalyst.

From the temporal and thermal changes of gel structure, CH_3COO, H_2O and OH were the organic materials which reside in the gel to the last. The FT-IR spectra of the gel aged for 3 years suggested that the gelation time of PZT system is far longer than that of the other systems such as TiO_2, ZrO_2 and $PbZrO_3$ at room temperature. The stock solution with 2 mol H_2O+0.2 mol NH_4OH showed the fastest gelation rate at room temperature.

Figure 10. FT-IR spectra of the gel as a function of heat treatment temperature (a) 100 °C, (b) 140 °C, (c) 250 °C, (d) 400 °C, (e) 550 °C, (f) 700 °C (gel was heated for 2 hours at each temperature).

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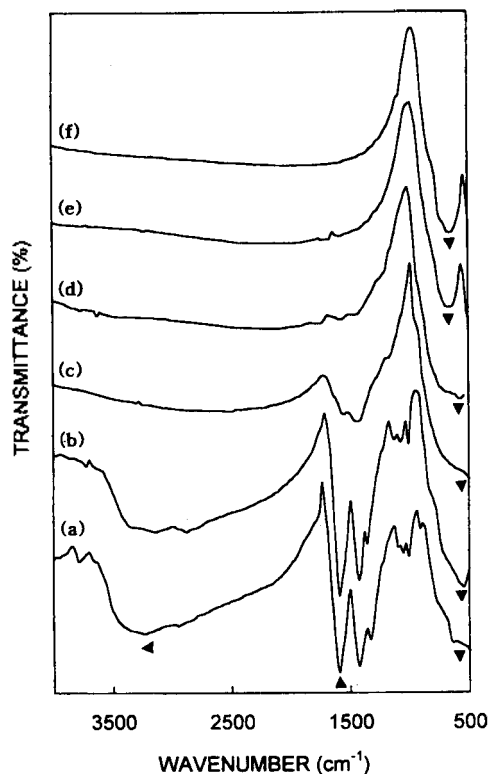
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Thermo-Physical Properties of Some Coumarin Complexes

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A number of complexes of transition metal ions with some coumarin derivatives have been prepared and their structures were elucidated with the help of conductometric, photometric and infrared studies. The stability constants of various complexes were determined, in aqueous medium, at different temperatures potentiometrically. The thermodynamic characteristics, ΔG, ΔH and ΔS, were calculated. The electrical behaviour of prepared compounds was followed.

Introduction

An increased interest in coumarin chemistry is mainly due to a wide spectrum of their biological activities. The coumarin skeleton is related to many natural products, *e.g.*, the Umbelliferae and Rutaceae families, and drugs, *e.g.* antifungi, carcinogenics and anticoagulatives. Consequently, synthesis and reactivity of coumarins have been extensively studied.[1-4] The structures were established by spectroscopical techniques.

As a part of the ongoing interest in the area of physical properties of complexes, a number of some substituted coumarins were complexed with different transition metal ions and their thermodynamic characteristics were studied. Potentiometric, conductometric, photometric and spectral techniques were used in this work. The electrical conductivity of solid samples was also investigated.

Experimental

All the chemicals used were of AR grade. Details of the

preparation of coumarin derivatives used in the present study are the same as reported previously.[5-8] The prepared coumarins have the following structures:
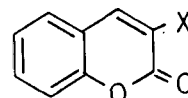
Ligand I : X=NH₂   Ligand III : X=CN
Ligand II : X=OH   Ligand IV : X=COOC₂H₅

All potentiometric measurements were made with a digital pH-meter 5800-05 solution analyzer, Cole Parmer, with a glass calomel electrode assembly. Solutions of the different ligands were prepared in hot ethanol. Three titrations, *viz.* titration of a) free hydrochloric acid, b) free acid plus coumarin, and c) free acid plus coumarin plus the metal ion, were carried out in aqueous medium against 0.01 M KOH at 298, 313 and 323 K, respectively. Initial ionic strength of all the solutions was maintained at 0.1 M by adding requisite amounts of KCl. The stability constants were calculated according to the Irving and Rossotti's method.[9]