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¹H and ¹³C NMR Investigations of Pb(Zr,Ti)O₃ Thin-Film Precursor Solutions

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Solvent reactions, ligand substitutions, and the oligomer/polymer backbone structure are important factors in the solution preparation of ceramic films. In this study we have used ¹H and ¹³C NMR spectroscopy to characterize solvent and ligand effects in precursor solutions used for the deposition of ferroelectric PZT (lead zirconate titanate) thin films. Solutions were prepared by a sequential precursor addition method from carboxylate and alkoxide precursors of the three cations, and the solvents, acetic acid, methanol, and water. The results indicate that acetic acid was a key component in the solution preparation process. As observed previously for single metallic component systems, its presence resulted in esterification reactions, leading in the present case to the formation of methyl, isopropyl, and *n*-butyl acetates. Second, acetic acid functioned as a chemical modifier, or chelating agent, replacing essentially all of the alkoxy ligands of the original precursors. Since alkoxy replacement appeared to be complete, we may describe the PZT species formed in solution as oxo acetate in nature. Finally, the solvent and ligand behavior of a solution prepared by an inverted mixing order was compared to the behavior of the solution prepared by a sequential precursor addition. The spectra for the two solutions were similar, and only differences in the relative intensities of the ester and alcoholic resonances were observed.

I. Introduction

Lead zirconate titanate (PZT) thin films are currently under investigation for a number of applications, including: decoupling capacitors,[1] DRAMs,[2] nonvolatile memories,[3] optical storage media,[4] pyroelectric IR detectors,[5] and piezoelectric micromotors.[6] Both physical and chemical methods of deposition have been used for film fabrication. Physical deposition methods that have been utilized include sputtering,[7,8] molecular beam epitaxy,[9] ion beam deposition,[10] and laser ablation.[11] The chemical (solution deposition) methods that have been employed include sol-gel[12-14] and MOD (metalloorganic decomposition).[15-17] The use of solution deposition methods for PZT film fabrication is of interest because of enhanced compositional control compared to sputtering and other physical methods of deposition, ease of process integration with standard semiconductor manufacturing technology (typically, films are deposited using a standard photoresist spinner), and comparatively low capital investment costs.

The solutions used for deposition of PZT thin films usually employ metal carboxylate, M(OOCR)$_x$, and metal alkoxide, M(OR)$_x$, precursors; where R is an alkyl group and x is the valence of the metal species. To prepare a solution, the lead, zirconium, and titanium precursors are mixed and, in some cases, reacted in a mutual solvent. To date, three classes of solution preparation processes have found widespread usage. They are as follows: (i) the MOD process, initially developed by Vest and co-workers,[15] which utilizes precursors with large carboxylate ligands, such as neodecanoates and ethylhexanoates, and solvents such as xylene; (ii) a sol-gel approach developed by Budd and co-workers,[12] which uses 2-methoxyethanol as a solvent, and allows for the replacement of the original alkoxy ligands of the zirconium and titanium precursors by methoxyethoxy ligands under controlled conditions; controlled amounts of water are subsequently added to initiate hydrolysis and condensation; (iii) a sol-gel method developed by Sayer and co-workers,[14] which utilizes acetic acid and alcohols, such as propanol or methanol, as solvents.

The deposition and heat treatment processing steps for films prepared by these approaches are similar. In general, wet films are first deposited by either spin-casting or dip-coating. The films are then subjected to low-temperature (300-400 °C) heat treatment for organic pyrolysis, followed

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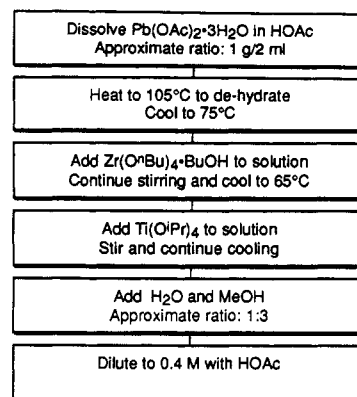(17) Haertling, G. H. *Ferroelectrics* **1991**, *116*, 51.

by high temperature (550–700 °C) heat treatment for densification and crystallization into the perovskite structure. Individual layers are typically 100–200-nm in thickness and are subjected to the organic decomposition process prior to the deposition of subsequent layers. Multiple layers are typically deposited to increase the final film thickness.

To date, studies of solution chemistry effects in PZT thin film processing have been relatively limited, and most have focused on characterization of solution reactions, and the nature of the solution polymeric species formed in the methoxyethanol-based sol–gel process.[18–21] However, PZT film fabrication based on processes that employ acetic acid are also widely employed. Because of the widespread use of these types of processes, in the present paper we detail our ^{1}H and ^{13}C NMR observations on the solvent and ligand aspects of a solution prepared by a sequential precursor addition (SPA) method. The results indicate that acetic acid was a key component in the solution preparation processes. As observed previously for single metallic component systems, its presence resulted in esterification reactions, leading, in the present case, to the formation of methyl, isopropyl, and *n*-butyl acetates. Second, acetic acid functioned as a chemical modifier, or chelating agent, replacing essentially all of the alkoxy ligands of the original precursors. Since alkoxy replacement appeared to be complete, we may describe the PZT species formed in solution as oxo acetate in nature.
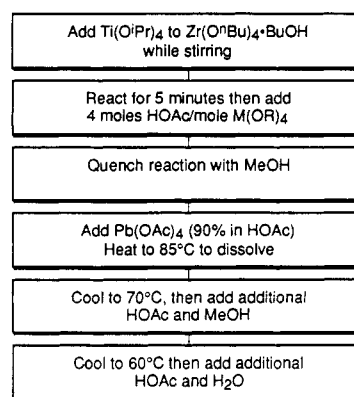
Finally, the solvent and ligand behavior of a solution prepared by an inverted mixing order (IMO) method was compared to the behavior of the solution prepared by a sequential precursor addition. In our preparation of PZT thin films, we found that the films prepared from these different precursor solutions displayed dramatically different microstructures and dielectric and ferroelectric properties.[13] Further, these films were prepared identically except for the solution preparation phase of the fabrication process; i.e., the films were deposited, organic constituents were removed and films were crystallized under identical conditions. This indicates that differences induced in the films during the initial solution preparation phase of the process persist in the final microstructure of the ceramic film. We found that the spectra for the two solutions were similar, and only differences in the relative intensities of the ester and alcoholic resonances were observed. These results indicate that polymer backbone effects are more likely responsible for the observed differences in film microstructure and electrical properties.

II. Experimental Section

Solution Preparation. Precursor solutions for PZT thin film fabrication were prepared by the two approaches outlined in Figure 1. For films prepared by both methods, the material composition was PZT 53:47 with 5 mol% excess lead ($Pb_{1.05}Zr_{0.53}Ti_{0.47}O_3$). In general, for both processes, 0.4 M (in PZT), 50-mL solution batches were prepared. For solution preparation by the first method (Figure 1a), the lead, zirconium, and titanium precursors were added sequentially to the solution. This sequential precursor addition (SPA) method is a modification of an approach originally reported by Sayer and co-workers.[14] Under

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(a)

(b)

Figure 1. Flow diagrams for (a) sequential precursor addition (SPA) process and (b) inverted mixing order (IMO) process.

ambient conditions, 7.966 g of lead(II) acetate trihydrate (Aldrich Chemical Co., Milwaukee, WI) was added to 3.98 mL of acetic acid (Aldrich). The solution was then heated to 105 °C for dissolution and dehydration of the lead acetate. Approximately 10 min was required to bring the solution to the boiling point. After holding the solution at 105–106 °C for 2 min, the heat source was removed and solution cooling was initiated by turning off the hot plate. At a temperature of 75 °C (approximately 25 min into the preparation), 4.85 mL of zirconium butoxide (80% in *n*-butanol (Aldrich)) was added to the solution. This resulted in an exothermic reaction and a temperature increase of about 10 °C. After approximately another four minutes, the solution temperature reached 65 °C, and 2.80 mL of purified titanium isopropoxide (Aldrich) was added.[22] Another slight exothermic reaction was observed. After another 2–3 min, the solution temperature decreased to 60 °C. At this point, the total solution volume was increased to 35 mL by the addition of a 3:1 (v/v) methanol–water mixture. After waiting approximately 8 min, solution preparation was completed with the addition of 15 mL of acetic acid. The solution was stirred throughout the entire process.

In the second approach (Figure 1b), an inverted mixing order (IMO) method was used. The first part of the process was carried out under inert atmosphere conditions. Following addition of acetic acid, solution preparation was completed under ambient laboratory conditions. (Other solution preparations carried out completely under ambient laboratory conditions yielded no significant differences in the corresponding film properties). Purified titanium isopropoxide (2.80 mL) was added to 4.85 mL of zirconium butoxide (80% in *n*-butanol). This resulted in an exothermic reaction and an approximately 10 °C rise in temperature. After 5 min, the temperature had decreased to about 30 °C, and 4.93 mL of acetic acid was added to the mixed alkoxide solution. This again resulted in an exothermic reaction and

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another 10–11 °C temperature rise. After waiting 6 min, 9.85 mL of methanol was added to the solution. At this point the solution temperature had decreased to 30 °C. After another 5 min, 10.34 g of lead (IV) acetate (Alfa Products; Ward Hill, MA) (90%) was added and the solution was heated to ~85 °C to dissolve the lead precursor. Complete dissolution required about 16 minutes. At this point the hot plate was turned off, and 10 mL of methanol were immediately added to rapidly decrease the solution temperature to ~70 °C. This was followed with successive additions of 5 mL of acetic acid, 10 mL of methanol, and 5 mL of acetic acid at 2-min intervals. During these additions the solution temperature gradually decreased to ~60 °C. After 5 min more, approximately 6 mL of deionized water was slowly added to the solution. During this time, the solution temperature decreased to ~50 °C. Stirring was maintained throughout the entire preparation process. It should be noted that in addition to inverting the mixing order of the three cation precursors, the IMO process uses a different lead precursor (lead tetraacetate) and slightly different solvent ratios than the SPA process.

Dried powder samples of each solution were also prepared. For the SPA solution, the sample was prepared by halting the preparation process following the addition of the titanium isopropoxide and vacuum distilling near room temperature for removal of solvent and byproduct components. The dried powder specimen of the IMO solution was again prepared by vacuum distillation at room temperature; however, in this case, the original solution preparation process was taken to completion.

NMR Characterization. The ¹H and ¹³C solution spectra were acquired on an IBM AC-200 spectrometer operating at 200 MHz ¹H. Tetramethyl silane (0.0 ppm) was used as a primary reference standard, with acetone (2.19 ppm) used as a secondary reference standard in some of the samples. Spectra were accumulated at ambient temperature, in a 5-mm probe. The ¹³C NMR spectra of the solid samples was recorded on a Chemagnetics console interfaced to a Nicolet 1280 data system. The samples were spun at 4.2 kHz at the magic angle in a 7-mm ceramic probe. The ¹H decoupling power was 35 kHz.

III. Results and Discussion

¹H NMR Characterization of the Precursor Solvents. We have used ¹H and ¹³C NMR to study the solvent and ligand aspects of a solution prepared by the SPA method. Shown in Figure 2 is the ¹H spectrum of the SPA solution, in both full and expanded scales. The most intense peaks are due to the solvents, methanol and water, and XOAc, where X is a proton, metal cation or an alkyl group. The intense peaks are labeled in the full scale spectrum (Figure 2a), and assignments for each of the peaks are given in Table I. Peak assignments are based on comparison of measured chemical shifts with chemical shift values reported in the literature[23,24] and on the results of doping experiments; i.e., experiments in which additional amounts of a component were added to the sample and an increase in a resonance or set of resonances was monitored.

A predominant feature of the spectrum is the splitting of the XOAc resonance into narrow and broad components. A doping experiment with acetic acid resulted in an increase in the intensity, a slight downfield shift and a narrowing of the broad component at 2.01 ppm. Since the proton (and the ¹³C) resonance is very symmetrical, we believe that it is unlikely that the linewidth can be attributed to inhomogeneous broadening (i.e., a "composite" resonance which is a superposition of several resonances with slightly different, but overlapping, chemical shifts). We believe that the resonance is broad because
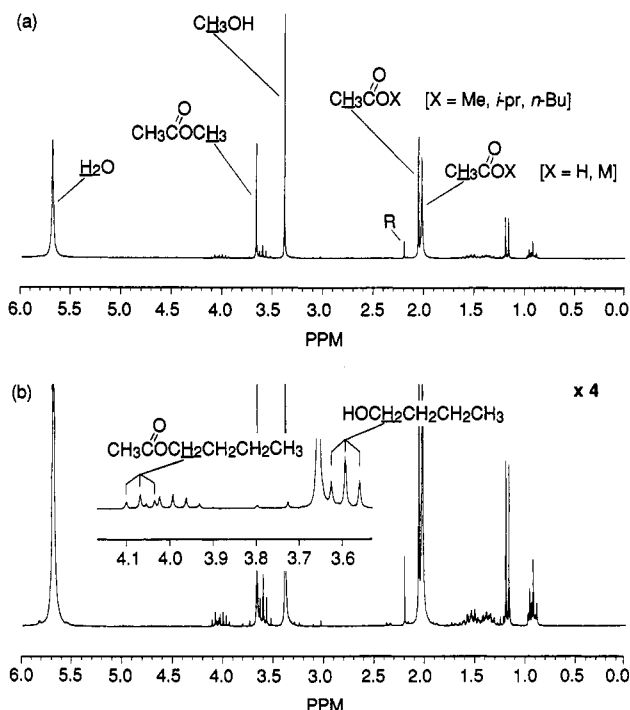
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(24) Pouchert, C. J. *The Aldrich Library of NMR Spectra*, 2nd ed.; Aldrich Chemical Co.: Milwaukee, 1983.

Figure 2. ¹H NMR spectrum of the SPA solution: (a) normal; (b) expanded. A small amount of acetone was added as a reference.

Table I. Experimental and Reported ¹H Chemical Shifts for Water, Acetic Acid, Alcohols, and Esters Present in the SPA Solution (Peaks Are Singlets unless Otherwise Noted)[e]
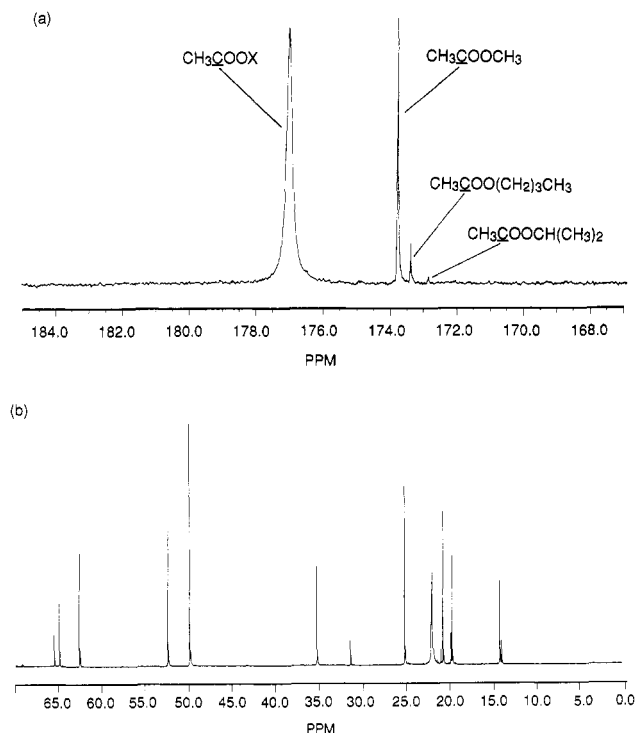
		exptl (ppm)	lit. (ppm)
H₂O, ROH[a]		5.57	
acetic acid	CH₃COOH	2.01	2.10[c]
methanol	CH₃OH	3.37	3.47[c]
isopropyl alcohol	(CH₃)₂CHOH	3.98 (h)	4.00[c]
	(CH₃)₂–	1.17 (d)	1.20[c]
n-butanol	CH₃(CH₂)₂CH₂OH	3.59 (t)	3.66[d]
	–(CH₂)₂–	1.3–1.6 (m)	
	CH₃–	0.91 (t)	0.93[d]
methyl acetate	CH₃O₂CCH₃	3.65	3.71[d]
	–CH₃	2.04	2.10[d]
isopropyl acetate	(CH₃)₂CHO₂CCH₃	4.98 (h)	5.02[d]
	(CH₃)₂–	1.22 (d)	1.25[d]
	–O₂CCH₃	(~2.04)[b]	2.04[d]
n-butyl acetate	CH₃(CH₂)₂CH₂O₂CCH₃		
	–CH₂O₂–	4.07 (t)	4.05[c]
	–(CH₂)₂–	1.3–1.6 (m)	
	CH₃–	0.93 (t)	0.95[c]
	–O₂CCH₃	(~2.04)[b]	2.03[c]

[a] Includes both alcoholic and acidic hydrogens. [b] Peak hidden by methyl acetate peak at 2.04 ppm. [c] Reference 23. [d] Reference 24. [e] Multiplicity: (d) = doublet; (t) = triplet; (h) = heptet; (m) = multiplet.

it corresponds to both free acetic acid and acetate ion which is chelated with a metal. The single broad line that is observed indicates that the ligand exchanges position on a frequency scale comparable to the difference in chemical shift between the hydrogens in free acetic acid and in acetate ions which are chelated with a metal. Based on chemical shift differences of hydrogens in similar positions on alkoxy ligands, we expect that the exchange frequency is on the order of 100 Hz. Conversely, the very narrow resonances observed for all of the alkoxy species imply that alkoxy moieties are not associated with the metal ions. Further evidence for the complete replacement

(a)

(b)

Figure 3. ^{13}C NMR spectrum of the SPA solution: (a) carboxylic region; (b) aliphatic region.

Table II. Experimental and Reported Proton Decoupled ^{13}C Chemical Shifts for Acetic Acid, Alcohols, and Esters Present in the SPA Solution

|		exptl (ppm)	lit.[a] (ppm)
acetic acid	CH_3CO_2H	176.8	175.7
	CH_3-	21.9	20.3
methanol	CH_3OH	49.8	50.5
isopropyl alcohol	$(CH_3)_2CHOH$	64.7	64.7
	$(CH_3)_2-$	25.1	26.5
n-butanol	$CH_3(CH_2)_2CH_2OH$	62.4	62.9
	$CH_3CH_2CH_2-$	35.2	36.0
	CH_3CH_2-	19.6	20.3
	CH_3-	14.1	15.2
methyl acetate	$CH_3O_2CCH_3$	52.3	51.5
	$-O_2CCH_3$	173.6	171.3
	$-O_2CCH_3$	20.6	20.6
isopropyl acetate	$(CH_3)_2CHO_2CCH_3$		
	$(CH_3)_2CH-$	69.0	67.5
	$(CH_3)_2-$	20.9	21.8
	$-O_2CCH_3$	172.7	170.4
	$-O_2CCH_3$	20.6	21.4
n-butyl acetate	$CH_3CH_2CH_2CH_2O_2CCH_3$		
	$CH_3CH_2CH_2CH_2-$	65.3	63.1
	$CH_3CH_2CH_2-$	31.3	30.4
	CH_3CH_2-	19.7	18.6
	CH_3-	13.9	12.7
	$-O_2CCH_3$	173.2	169.1
	$-O_2CCH_3$	20.6	19.4

[a] Reference 25.

of alkoxy ligands by acetate ligands will be presented in the following sections.

The narrow component of the XOAc resonance arises from the acetate groups of the ester compounds formed by esterification, i.e., the reaction of acetic acid with the methanol, isopropyl alcohol and n-butanol species present (see discussion below). The observed intensity of the narrow component is also in agreement with that expected on the basis of a peak integration of the alkyl resonances of the three ester compounds. The reaction of acetic acid with alcoholic species that leads to ester formation is shown in eq 1, where R is an alkyl group, in the present case, methyl, isopropyl, or n-butyl.

$$ROH + CH_3COOH \rightarrow ROOCCH_3 + H_2O \qquad (1)$$

In Figure 2b, the spectrum has been expanded vertically by a factor of 4, and a portion (the insert showing the spectral region from ~3.5 to 4.2 ppm) has also been expanded horizontally. In the expanded spectrum we can see that the alcoholic resonances also have both major and minor components. For the methyl protons, the resonance of the minor component appears ~0.3 ppm downfield from the primary methanol peak. For butanol, the methylene proton resonance (i.e., the resonance for the protons nearest the oxygen) has minor components at ~0.4 ppm downfield from the primary methylene peaks (see insert, Figure 2b). These minor resonances are due to methanol and n-butanol which have reacted with acetic acid to form methyl and n-butyl acetate, respectively. Assignment of these peaks is based on both comparison with reported literature values, shown in Table I, and doping experiments.

Ester formation can also be established by careful observation of the resonance for the methyl group of butanol. The methyl group resonance of the ester butoxy is shifted ~0.02 ppm downfield from the methyl group resonance of butanol. The two triplets can be assigned on

the basis of their intensities, and by adding additional butanol to the solution, which contributed to the intensity of the larger triplet.

^{13}C NMR Characterization of the Precursor Solvent. Portions of the proton decoupled ^{13}C spectrum of the SPA solution are shown in Figure 3. These areas contain all of the detectable resonances for the experimental conditions employed. Resonances for alcohols, ester compounds, and chelated acetate ligands were again observed. The addition of n-butanol or isopropyl alcohol to the solution resulted in no change in the widths or chemical shifts of the corresponding resonances, implying that the alcoholic resonances are indeed due to free alcohol, and not due to bound alkoxy groups. The ^{13}C NMR spectra of the solution-derived powders, to be discussed in the next section, provide further evidence that significant quantities of metal-bound alkoxy ligands are not present in these solutions. As with the ^{1}H spectrum, the peaks for the alcohols were split into major and minor components, and the minor components could be identified as the corresponding ester compounds. The ^{13}C resonances of the esters are narrow, well-resolved lines. Thus, the esters, once formed, do not undergo further exchange. The resonances were assigned on the basis of comparison with chemical shifts reported in the literature,[25] doping experiments, and comparing peak intensities of carbons from the same species. Peak assignments are reported in Table II.

The ^{13}C spectrum also displayed splitting of the XOAc resonance into narrow and broad components. In the proton and aliphatic region, two XOAc resonances, a sharp peak at 20.6 ppm and a broad peak at 21.9 ppm, were observed. In the carboxy region of the spectrum, four resonances, sharp peaks at 173.6, 173.2, and 172.7 ppm and a broad peak at 176.8 ppm, were observed. Examination of the ^{1}H and aliphatic regions of the spectrum have shown that the relative concentrations of the esters are methyl acetate > n-butyl acetate > isopropyl acetate. The three narrow peaks in the carboxy region of the
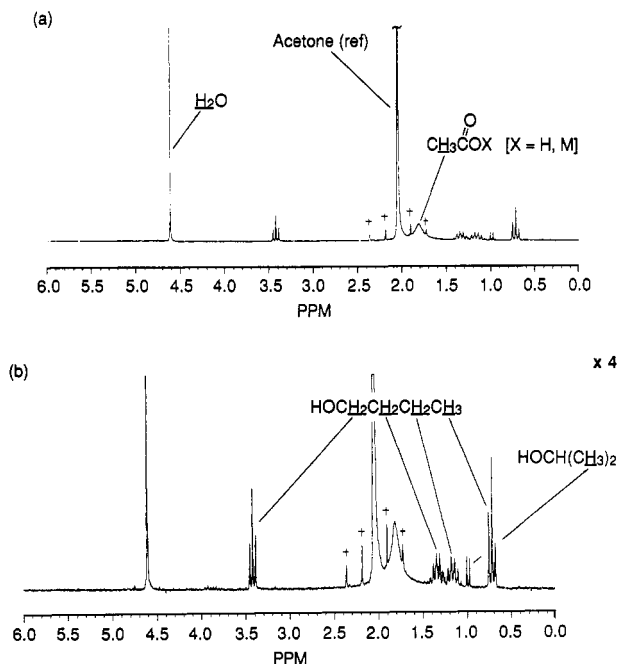
Figure 4. ¹H spectrum of dried SPA solution redissolved in D₂O: (a) normal and (b) expanded. A small amount of acetone was added as a reference. The acetone peak is more intense than the peaks due to the sample since the dried powder was only partially soluble in D₂O. The peaks marked with a cross are spinning sidebands.

spectrum are of the appropriate intensities, and thus correspond to the three esters, as assigned. The broad peak at 176.8 ppm is therefore due to free acetic acid and the acetate ligand. Addition of acetic acid to the sample resulted in an increase in the intensity of the broad resonances at 21.9 and 176.8 ppm, again confirming the assignments of these two resonances.

¹H and ¹³C NMR Characterization of the Ligand Substitution Process. In addition to studying the nature of the reactions and reaction byproducts of the solution preparation process, we are also interested in describing the nature of the ligand substitution process. We have thus looked at samples from which the majority of the solvents and by-products have been removed. The spectrum shown in Figure 4 is for a sample that was prepared by halting the SPA solution preparation following addition of the titanium precursor, and removing, by vacuum distillation near room temperature, any byproducts which might have been formed. The dired solid thus obtained was redissolved in D₂O, and the ¹H NMR spectrum was then acquired. The spectrum for this sample is characterized by intense peaks due to water and acetate. While part of the intensity of the water peak is expected to be due to the protio impurities in the D₂O solvent, another contribution to this peak is water generated via eq 1 which was not removed by the distillation process, due to its lower volatility. From a comparison of Figure 4 with Figure 2, it is evident that the minor components of the methyl, n-butyl, and isopropyl resonances are no longer present, indicating complete removal of the ester compounds. This is expected because of the comparatively high volatility of these materials. Further study of the two spectra shows that methanol has also been completely removed, and that the concentration of isopropyl alcohol is now much lower than n-butanol. This trend is also expected from the relative volatilities of the three alcohols; methanol > isopropyl alcohol > n-butanol.
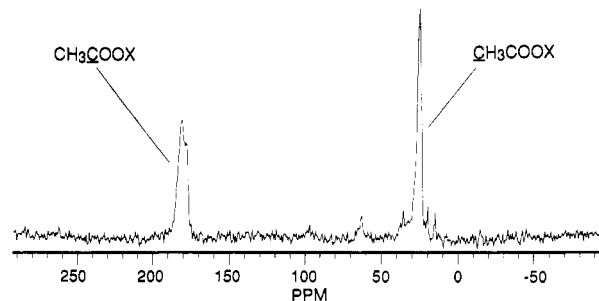
Figure 5. ¹³C solid-state NMR spectrum of SPA-derived powder prepared by drying under vacuum.

Also in this spectrum, the XOAc (X = H or metal) resonance is significantly broader than in the spectrum of the neat solution. Since the room temperature volatility of acetic acid is between that of n-butanol and isopropyl alcohol, we suspect that most of the free acetic acid has been removed during the vacuum distillation, and the remaining acetic acid is present in the form of acetate chelated to metals. Addition of a small amount of acetic acid to the sample narrows and shifts the XOAc resonance considerably.

Compared to the acetate resonance, the resonances for isopropyl alcohol and n-butanol are narrow. Further, the width and position of the butanol resonances do not vary with the addition of butanol to the sample, which indicates that they are due to free butanol and not to bound butoxy ligands. The implications of these results regarding the nature of the solution polymeric species formed are discussed further below.

We further characterized the nature of the ligand substitution process with solid-state ¹³C NMR of solution-derived powders. Results are presented in Figure 5 for a powder that was obtained by drying the SPA solution under vacuum for 3 h at 40 °C. As with the sample used for the ¹H spectrum illustrated in Figure 4, this sample should also be essentially composed of the polymeric PZT species that is formed during the solution preparation process, since the reaction byproducts and solvents have been removed. The spectrum was accumulated using cross-polarization (CP) and magic angle spinning. Although CP spectra are not quantitative, we expect that this spectrum will provide relatively accurate peak intensity ratios, because the peak intensities exhibited a broad maximum as a function of CP time. The CP time shown, 3 ms, was chosen to be near the center of this broad maximum. Two primary peaks, at 181 and 25 ppm may be assigned to the acetate ligand.[25] Since this sample is a solid, it is not surprising that the resonances are shifted several ppm from the resonances observed for the solution sample due to sample susceptibility effects. The carboxy resonance consists of a primary peak at 181 ppm and a secondary peak at 178 ppm. We believe that the complex nature of this resonance, and its broadness, is indicative of the acetate ligand bonding to different metals and the possibility of both uni- and bidentate bonding.

Several minor resonances are also present in the ¹³C aliphatic region. The peaks at 14, 20, 35, and 62 ppm are similar to the resonances of free butanol and/or butoxy ligands. We believe that these resonances are not caused by species complexed with metals, however, because they are considerably sharper than the resonances of the bound

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Table III. Analysis of Ester Formation for SPA and IMO Precursor Solutions

reactant	mmol of reactant	fraction reacting → ester	mmol of ester formed
		SPA Solution	
Bu^nOH	57.24	0.23	13.2 (*n*-butyl acetate)
Pr^iOH	37.60	0.05	1.9 (isopropyl acetate)
MeOH	370.30	0.32	118.5 (methyl acetate)
	total ester formation: 133.6 mmol		
	(water formation: 6.7 mol of H_2O/mol of $M(OR)_4$)[a]		
		IMO Solution	
Bu^nOH	57.24	0.20	11.4 (*n*-butyl acetate)
Pr^iOH	37.60	0.03	1.1 (isopropyl acetate)
MeOH	588.80[b]	0.16	94.2 (methyl acetate)
	total ester formation: 106.7 mmol		
	(water formation: 5.3 mol of H_2O/mol of $M(OR_4$)[a]		

[a] Water formation calculated from eq 1, measured ester formation, and known quantities of alkoxide reactants. [b] See discussion in text regarding determination of mmol of methanol available as a reactant.

acetate ligand. The integrated area of the minor resonances is approximately 6% of the area of the acetate ligand resonances. Traces of residual *n*-butanol may not have been removed during vacuum drying because of its low volatility. A small amount of isopropyl alcohol could also be present in this sample but confirmation of its presence is not possible because its resonances would be hidden by the methyl group of the acetate ligand and by the butanol resonance at 62 ppm. Even if these resonances are due to alkoxy ligands, and not free alcoholic species, the comparatively low intensity of these peaks indicates that essentially all of the original alkoxy ligands of the starting precursors have been replaced by chelated acetate groups. Therefore the primary polymeric species formed in each of the two processes is oxoacetate, and not oxo acetate alkoxide or oxo alkoxide, in nature. The solid-state ^{13}C NMR investigations thus yielded similar results regarding the nature of ligand substitution as the ^1H study of the redissolved SPA-derived powder.

Comparison of the SPA and IMO Preparation Processes. The characteristics of the ^1H NMR spectrum of the IMO solution were identical in terms of the number and position of the resonances observed, indicating that the local chemical environments of the protic species are the same for both solutions. There were, however, differences in the relative peak heights (ester/alcohol), which imply differences in the quantities of byproducts in the two solutions. We have analyzed the differences in the amounts of esters formed, and the results are presented in Table III. (An identical analysis can be carried out on the corresponding ^{13}C spectra, yielding analogous results.) In this table, the millimoles of alcoholic reactants present were calculated assuming that all of the alkoxy groups of the precursor alkoxides were free to react with acetic acid. The relative amounts of alcohols which underwent esterification in the SPA solution are 32, 5 and 23% for methanol, isopropyl alcohol, and *n*-butanol, respectively. The amount of each ester formed depends on the initial concentration of the respective alcohol, and the percentage which underwent esterification. For the SPA solution, the relative amounts of esters formed are 100:1.6:13 for the methyl acetate, isopropyl acetate, and *n*-butyl acetate, respectively, and total ester production was calculated to be 134 mmol. Considering that there are only 20 mmol of PZT in the solution for the volume prepared, this is a relatively significant amount of byproducts.

Esterification analysis of the IMO solution is more complicated than for the SPA solution. Due to their low volatilities and higher boiling points, we expect the results for the *n*-butanol and isopropyl alcohol alcoholic fractions reacting (to form the corresponding esters) to be reasonably quantitative. However, because of the volatilization of methanol and methyl acetate that occurs when the solution is heated to 85 °C for dissolution of the lead, analysis of methyl acetate formation for this solution therefore requires an estimate of the amount of methanol removed by volatilization. By comparing the solution volume before and after lead dissolution, we estimate the amount of methanol that has volatilized as ~6 mL. This results in ~588 mmol of methanol remaining as a reactant. Using these assumptions, analysis of the chemical composition of the final IMO solution indicates that the alcohols in the IMO process have undergone less esterification than in the SPA process. In the IMO process, the ratio of Me: *i*-Pr:*n*-Bu acetates remaining in the solution was 100:0.3: 11. Total ester content for the final IMO solution was calculated to be 107 mmol. Due to the assumptions involved with methanol esterification it is difficult to state unequivocally whether the amount of esters formed in the two processes is significantly different. However, we may still state that for the final precursor solutions used for film fabrication, the SPA solution was characterized by a higher ester content than the IMO solution.

While comparison of the exact quantities of esters formed is difficult due to the assumptions required for the methanol and methyl acetate volatilization, another, potentially more important, observation for both solutions is the in situ formation of significant quantities of water, another byproduct of esterification, for both processes. While we intentionally add water to the solutions during the final stage of solution preparation, the presence of in situ generated water in the two processes is still expected to be important for two reasons. First, compared to the water which is intentionally added near the end of the two solution preparation processes (~260–330 mmoles), the amount of water generated in situ is significant (~107–134 mmol). Second, since it is generated earlier in the processes, if chelation of the original precursors by acetic acid is not yet complete, concurrent hydrolysis and condensation may be initiated.

The ligand substitution processes of the SPA and IMO preparation procedures were also compared. An aqueous solution was prepared from an IMO sample in which the solvents and byproducts were removed. The ^1H NMR spectrum of this liquid sample was similar to that of the corresponding SPA sample, indicating complete ligand substitution. This result was confirmed by the ^{13}C solid-state spectrum of the IMO derived powder. The spectrum displayed exclusively the two major acetate resonances; no resonances for trace solvents were observed.

IV. Conclusions

Our NMR studies indicate that, under the present preparation conditions, acetic acid acts as more than a simple solvent for dissolving the lead precursor. First, acetic acid undergoes an esterification reaction with the alcoholic species in solution as shown by eq 1. This reaction leads to the formation of methyl, isopropyl, and *n*-butyl acetates as well as the generation of water. Second, as reported previously for single metallic component systems,[26,27] in the processing of multimetallic component

PZT solutions, acetic acid also acts as a chemical modifier (i.e., a chelating agent) changing the nature of the precursors on a molecular level.[26-29] Although Larbot[27] found only partial replacement of the alkoxy group on zirconium, we found that the alkoxy group was completely replaced by the acetate group in a the PZT system. Doeuff[28] also found complete replacement of the alkoxy group for a titanium-based system.

From the present NMR study, it is not possible to describe, in detail, the nature of the bonding between the acetate groups and the metal cations; i.e., whether the acetate groups are unidentate or bidentate and whether they are bridging between like or dissimilar cations. The broad resonance in the carboxy region of the solid-state ^{13}C spectrum would seem to indicate that acetates in more than one environment are present. This result is in agreement with FTIR spectroscopy studies, which indicated that more than one acetate coordination environment was likely.[13]

While the NMR results indicated that essentially none of the alkoxy ligands of the starting precursors remain in the final PZT solution precursor species, chelation may not be the only reaction responsible for alkoxy ligand substitution. In addition to alkoxy replacement, the alkoxy groups of the precursor alkoxides may also be replaced through hydrolysis and condensation. To determine unequivocally the importance of the two pathways leading to ligand substitution in the processing of these PZT solutions requires study beyond a "post-mortem" analysis of the identity and amount of esters present in the two solutions.

Comparable solvent reactions and ligand substitutions were occurring in the precursor solutions prepared by the two preparation procedures. While similar amounts of water were formed in the two processes, we might expect that depending upon when in the preparation scheme this water was generated, the relative importance of chelation vs hydrolysis and condensation could vary. Changes in this reaction pathway could affect the PZT solution polymeric species and impact the nature of the film. Other differences in the characteristics of the solutions, for example, the amounts of solvents and lead precursor used, may also be significant in defining subsequent structural evolution to the perovskite phase. Future studies will focus on the structure of the oligomer/polymer backbone.

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