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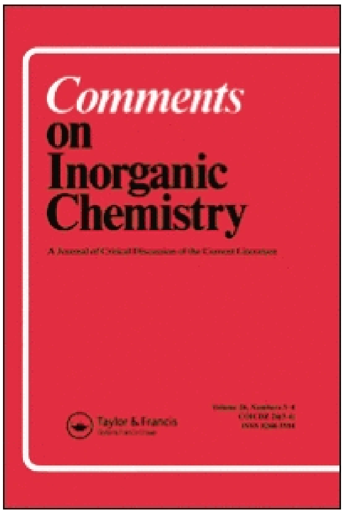

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An Investigation of Group (IV) Alkoxides as Property Controlling Reagents in the Synthesis of Ceramic Materials

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An Investigation of Group (IV) Alkoxides as Property Controlling Reagents in the Synthesis of Ceramic Materials

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Chemical synthetic methodologies are frequently employed to fabricate ceramic materials. To assist in determining methods for control over the final properties of ceramic materials, we have begun an investigation of the basic chemistry of sol-gel precursor solutions for lead zirconate titanate (PZT) thin films. The reactions between "$M(OCHMe_2)_4$" (M = Ti, Zr) and acetic acid were monitored by ^1H, ^{13}C, ^{17}O NMR, and X-ray crystallography. The results of this investigation, the complexes generated, ($Ti_6(OCHMe_2)_{12}(OAc)_4O_4$, **1**, $Ti_6(OCHMe_2)_8(OAc)_8O_4$, **2**), and the types of films produced are reported. The synthesis of novel Group (IV) metal alkoxide complexes has been undertaken to generate precursors for ceramic materials with the desired characteristics internalized. In an attempt to reduce hydrolysis, the formation of a variety of metallo-organic compounds containing the sterically bulky adamantan-1-ol ligand (AdamO-H) was studied. It was demonstrated that the $OCHMe_2$ ligands of "$M(OCHMe_2)_4$" (M = Ti, Zr) were easily replaced with AdamO, forming compounds with the empirical formula "$(AdamO)_nM(OCHMe_2)_{4-n}$" ($n = 1, 2, 3$, or 4). Spin-cast deposited films of these compounds were not affected by ambient humidity and crystallize upon evaporation of the solvent. Another set of alkoxide ligands which has been investigated is a series of tridentate alkyl alkoxides: 1,1,1-tris(hydroxymethyl)ethane (THME-H_3), 1,1,1-tris(hydroxymethyl)propane (THMP-H_3), 1,3,5-cyclohexanetriol (CYHT-H_3), and 2,2-bis(hydroxymethyl) proprionic acid (BHMP-H_3). These ligands have been

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reacted with Group 4 metal alkoxides to form a variety of precursors that have been identified by spectroscopic and analytical methods. The THME and THMP ligated complexes are of the general formula $(THMR)_2M_4(OCHMe_2)_{10}$ [R = E, M = Ti, **3**, and Zr, **4**; R = P, M = Ti, **5** and Zr]. Films of these compounds demonstrate reduced susceptibility to hydrolysis when compared to the standard starting materials $Ti(OCHMe_2)_4$, **6**, and $[Zr(OCHMe_2)_4 \cdot HOCHMe_2]_2$, **7**.

Key Words: *lead zirconate titanate, PZT, metal alkoxides, acetic acid, iso-propoxide, tridentate alkoxides, adamantan-1-ol, titanium, zirconium, lead, sol-gel*

Abbreviations:

PZT—lead zirconate titanate
$THME\text{-}H_3$—1,1,1-tris(hydroxymethyl)ethane
$THMP\text{-}H_3$—1,1,1-tris(hydroxymethyl)propane
$CYHT\text{-}H_3$—1,3,5-cyclohexanetriol
$BHMP\text{-}H_3$—2,2-bis(hydroxymethyl)proprionic acid
AdamO-H—adamantan-1-ol
HOAc—acetic acid
THF—tetrahydrofuran
TGA/DTA—thermal gravametric analysis/differential thermal analysis

INTRODUCTION

Metallo-organic alkyl alkoxides are used as precursors for ceramic materials that are employed in several areas of technology, ranging from single component silicate membranes for gas separation,[1] to multicomponent perovskite materials for thin film electronic memories.[2] The latter materials are most often based on lead zirconate titanate (PZT) due to its interesting dielectric and ferroelectric properties.[3] Accurate compositional control of these materials, and the possibility for uniform incorporation of small levels of dopant species, can be accomplished by solution deposition approaches. These "sol-gel" processes have found widespread use in the fabrication of multicomponent thin films compared to other "physical" deposition processes, such as sputtering.[4] Furthermore, solution deposition of these materials may be accomplished by spin-casting, a process widely utilized in standard semiconductor wafer fabrication.[5] Solution deposition of these metallo-organic carboxylates and alkoxide precursors, generally called the "sol-gel" process, has been shown to be advantageous in generating high quality ferroelectric PZT thin films.[6] Historically, PZT film fabrication by solution deposition has been undertaken using commercially available alkoxide and acetate reagents such as $Ti(OCHMe_2)_4$, $[Zr(O(CH_2)_3Me)_4 \cdot HO(CH_2)_3Me]$, and $Pb(O_2CMe)_2 \cdot 3H_2O$ to form the complex ceramic precursors.[4,6]

Interestingly, it has been observed that the electrical and microstructural properties of the films are dependent not only on the precursors employed, but also on a number of other factors, such as solution aging.[7] While these variations have often been attributed to differences in precursor characteristics, the exact nature of many of these compounds, such as the structure of the precursor in solution and/or the solid state, are not fully understood or known. Although high quality materials have been prepared using solution deposition approaches, limited understanding of the complex chemistry of the precursor solutions often causes problems with process control and reproducibility.[8] To fully develop this field, systematic studies on the effects of the precursor variations (i.e., ligands effects) on "structural evolution" (organic pyrolysis, film densification and crystallization) and an understanding of the interrelationships involved in sol-gel material processing must be developed. This information will ultimately lead to controlling the final properties of the ceramic materials generated and to successful production of thin film devices.

In 1978, Bradley and Mehrotra wrote what is considered the definitive book on metal alkoxides[9] and it has become the reference book of choice for a wide variety of chemists and materials researchers. However, this wealth of information has lead incorrectly to the assumption that the alkoxide field is fully understood. Often following what are considered traditional synthetic pathways to "pure" alkoxides, the expected product will not always be isolated. Instead, incorporation of O^{2-}, A^+(Li, Na, K), and X^-(Cl, Br, I) ions into the lattice of these metal alkoxide compounds is quite common.[10] The exact structure of these compounds has been determined by X-ray crystallographic studies. Furthermore, the structure of these metal alkoxide compounds has been proven to differ from the expected monomers and dimers. A couple of examples will demonstrate the validity of the above statements.

One compound that illustrates some of the problems associated with the synthesis of pure alkoxides is yttrium *iso*-propoxide, "$Y(OCHMe_2)_3$". This compound is commercially available,[11] has been known for decades, and is widely used for a variety of material applications, such as a precursor to the superconductor $YBa_2Cu_3O_{7-x}$.[12] However, the compound has been identified as $Y_5(OCHMe_2)_{13}O$.[13] The source of the oxide in this structure, and a number of other alkoxides, is not completely understood.[14] Furthermore, there is no known method for synthesizing the pure alkoxide "$Y(OCHMe_2)_3$". This observation goes hand in hand with other structurally characterized lanthanide alkoxides of the proposed formula: "$Ln(OCMe_3)_3$". It has been found that the classical metathesis of LnX_3 with NaOR produces compounds of the general formula: $Ln_3(OR)_3(\mu\text{-}OR)_3(\mu_3\text{-}OR)(\mu_3\text{-}X)X(S)_2$ (Ln = yttrium, lanthanum, or lanthanides; X = OR, or halide; S = THF or ROH).[14] This illustrates the increased nuclearity, oxide formation, and halide retention that many metal alkoxides undergo.

Another example of the retention of these types of ions is reactions involving the dimeric zirconium *iso*-propoxide, $Zr_2(OCHMe_2)_8(HOCHMe_2)_2$. If $[Zr(OCHMe_2)_4 \cdot (HOCHMe_2)]_2$ is reacted with one equivalent of potassium hydride, a simple alcoholysis occurs, followed by loss of two alcohols, and incorporation of a potassium atom into the structure, forming $KZr_2(OCHMe_2)_9$.[15] However, an additional equivalent does not form the di-substituted species; instead, it forms the compound $K_4Zr_2O(OCHMe_2)_{10}$.[16] This demonstrates the retention of alkali metals, formation of oxides, facile coordinated ligand exchange, and the diverse structural types available to these metal alkoxide compounds.

A final illustration of the problems associated with metalloalkoxides is the attempt to generate stoichiometric niobium/lead compounds. Such binary and ternary (Pb, Mg, Nb) compounds offer the possibility of compositional control at the molecular level,[10,17] and the ability to induce crystallization of thin films at comparatively low processing temperatures. Hence, these compounds are of immense technological interest. In particular, Nb/Pb and Mg/Pb compounds may serve as precursors for the fabrication of the high dielectric constant, relaxor ferroelectric material lead magnesium niobate or PMN $[Pb(Mg_{1/3}Nb_{2/3})O_3]$. Unfortunately, attempts to synthesize a mixed niobium–lead complex from the reaction of $Pb_4O(OEt)_6$ and $Nb_2(OEt)_{10}$ yields the condensed complex $Pb_6O_4(OEt)_4Nb_4(OEt)_{20}$,[10a,17,18] which occurs regardless of the Pb:Nb molar ratio used. This reaction illustrates the "sinks" which can occur in the solid state for reaction mixtures, regardless of the initial stoichiometries involved. The loss of the desired stoichiometry at the molecular level prohibits the use of these compounds as well-characterized precursors for film fabrication. Because these poly-metallic precursors are of such potential importance, however, reaction pathways from these "sinks" to alternative activated compositional states must be developed and understood.

As these examples demonstrate, the alkoxide field is not nearly as advanced as might be expected. It is important to recognize the need to further characterize metal alkoxides by finding consistent and general synthetic pathways. To do this, the basic chemistry of these reactions must be understood, and therefore, determination of the basic structural types is vital. These results must be correlated with solution molecular studies to determine what species are present in solution. Well characterized chemical pathways and compounds can then be utilized for the generation of internalized property-controlled materials. The surprising dearth of well-characterized "pure" alkyl alkoxides of Group 4 metal complexes necessitates the development of a data-base for structural and material interpretations to aid in tailor-making ceramic materials. Typically, in early transition metal chemistry the bis-cyclopentadienyl ligated complexes which are well-characterized have been frequently utilized[19]; however, due to the aromatic nature of these ligands, incomplete pyrolysis at elevated temperatures may occur.[6c] This leads to the investigation of alkyl alkoxide compounds, which, in contrast, have relatively low pyrolysis temperatures.[6c] Alas, when the steric bulk of the cyclopentadienyl ligands is removed and replaced with alkyl alkoxides, the structural composition of these compounds is dramatically altered.[9,10,17]

Definition of the relationships between precursor structure and the transformation behavior of the films remains to be accomplished. As part of an effort to develop this understanding, we have undertaken the synthesis of well-characterized metallo alkoxide precursors that are similar to standard starting materials but which have alterations in the ligands that will internalize the characteristics desired of the final thin film compounds. From these precursors we have prepared ceramic thin films and have attempted to relate observed variations in the films produced and the film densification behavior to the precursor properties. Some of the effects that we are attempting to control in our generated precursors include: limiting aging effects, reducing hydrolysis susceptibility, and controlling oligomerization. This report will summarize our initial investigations of the basic chemistry of "$M(OCHMe_2)_4$" and HOAc using ^{17}O NMR and X-ray crystallographic studies; endeavors to reduce reactivity of metal alkoxides with ambient humidity by addition of the sterically hindering ligand adamantanol; and attempts to relate structural aspects to film characteristics of these compounds using tridentate ligands.

DISCUSSION

I. Basic Sol-Gel Chemistry

I.1 Reaction of $Ti(OCHMe_2)_4/HOAc$-^1H, ^{17}O *NMR and X-Ray Studies*

Frequently, precursor solutions for sol-gel PZT thin films have been generated from metal alkoxides in acetic acid (HOAc).[6] We, therefore, have begun to investigate these *simple* reactions in an attempt to elucidate the time of formation of the products (i.e., aging effects) as well as the identity of pertinent precursors formed in these reactions. Understanding this aging process will ultimately aid in dictating the time allotted for product formation, as well as indicating the target molecules desired for tailor-made precursors. The *simple* reactivity between "$M(OCHMe_2)_4$" (M = Ti, Zr) and n HOAc, where n = 1 or 2 (Eq. (1)), is being investigated.

$$n\ \mathrm{HOAc} + \text{“}M(OCHMe_2)_4\text{”} \xrightarrow{\text{neat}} ??????$$

$$M = \mathrm{Ti, Zr} \qquad (1)$$

$$n = 1, 2$$

Sanchez *et al.*[17,20] have done an exceptional job in characterizing the initial products of the reaction between $Ti(OR)_4$ (R = $CHMe_2$ and CMe_3) and acetic acid (HOAc) as $Ti_6(OR)_{10}(OAc)_4O$. We are also interested in the exact nature and time of formation of transitory by-products and products of increased stoichiometry and varied metals.[21] Therefore, we have started to monitor these reactions by ^{1}H, ^{13}C, and ^{17}O NMR. Products were identified by NMR, FT-IR, thermogravimetric and differential thermal analysis (TGA/DTA), elemental analysis, and single crystal X-ray studies, when possible. Due to the high degree of oligomerization and disparate types of alkoxide ligands, we have run the same reactions with deuterated and enriched reagents to aid in elucidation of the number, types, and origin of the ligands present.

X-ray crystallographic studies were undertaken of the reaction product from Eq. (2a).

$$HOAc + Ti(OCHMe_2)_4 \xrightarrow{neat} Ti_6(OCHMe_2)_{12}(OAc)_4O_4 + \cdots \tag{2a}$$

This compound was formed under an inert atmosphere over an extended period of time. The product formed is $Ti_6(OCHMe_2)_{12}(OAc)_4O_4$, **1** (Fig. 1 is a ball stick representation of the crystalline complex isolated).[21] The structure of this compound is consistent with the complex found previously.[20a] From a reaction stoichi-

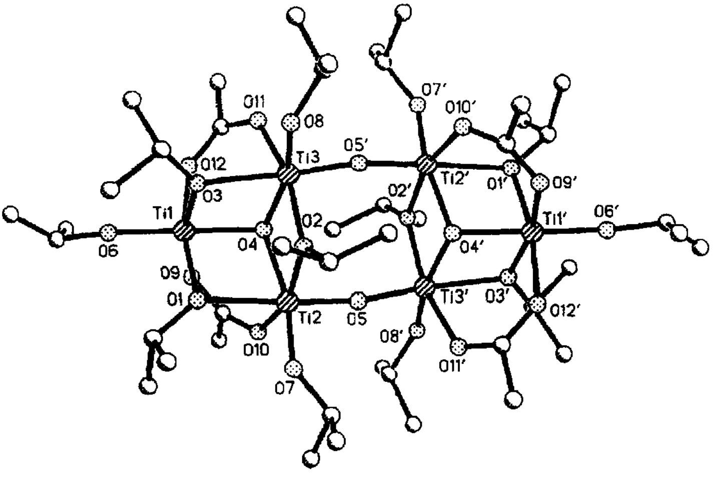


FIGURE 1 Ball and stick drawing of $Ti_6(OCHMe_2)_{12}(OAc)_4O_4$, **1**.

ometry of 1 to 2 $Ti(OCHMe_2)_4$ to HOAc (Eq. (2b)), we have recently isolated another compound, which is $Ti_6(OCHMe_2)_8(OAc)_8O_4$, **2**.[21]

$$2HOAc + Ti(OCHMe_2)_4 \xrightarrow{\text{neat}} Ti_6(OCHMe_2)_8(OAc)_8O_4 + \cdots \tag{2b}$$

Figure 2 is a ball stick representation of **2**. Both the 1 to 1 and 1 to 2 stoichiometries of the zirconium alkoxide and HOAc reaction products are being crystallized to determine the structure of these complexes.

To investigate the processes involved in the initial reaction phases of Eq. (2), a titration of $Ti(OCHMe_2)_4$ with HOAc in C_6D_6 was monitored by ^1H NMR spectroscopy. The reaction proceeds through several complex steps with each aliquot of HOAc added. Throughout the titration (n = 0 to xs), the mixture continues to react, wherein the $Ti(OCHMe_2)_4$ symmetry is destroyed coinciding with the appearance of a number of disparate methine and methyl peaks. An identical titration of $[Zr(OCHMe_2)_4 \cdot HOCHMe_2]_2$ with HOAc shows substantially different results when compared to the titanium data. After addition of the initial aliquots of HOAc, the ^1H NMR

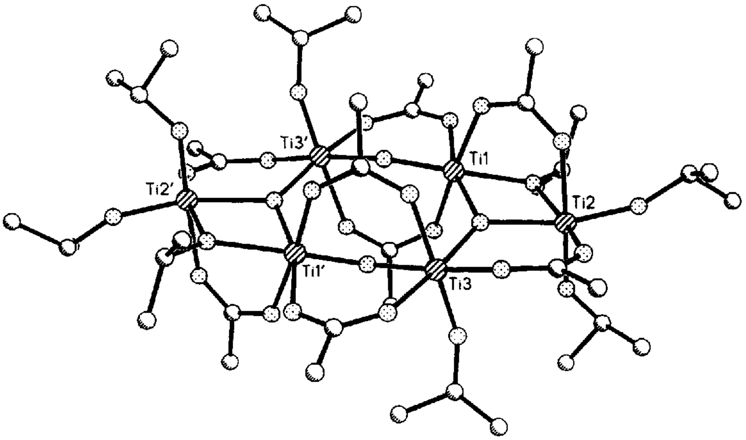


FIGURE 2 Ball and stick drawing of $Ti_6(OCHMe_2)_8(OAc)_8O_4$, **2**.

spectrum of the reaction mixture appears to be quite complex; however, with $n \geq 2$ there appears a symmetric product, which even with increased aliquots does not appear to undergo further transformation. Since the NMR spectra of these titrations become quite complex, the reactions were monitored, so that a time frame for formation and dissipation of intermediate species and the end point of the reaction could be determined.

The 1 to 1 titanium to HOAc reaction ($n = 1$) was followed by ^{1}H NMR over a two and one-half month period (selected spectra shown in Fig. 3). The initial peaks consist of the broad $Ti(OCHMe_2)_4$ and HOAc resonances as seen in the titration spectrum. As the

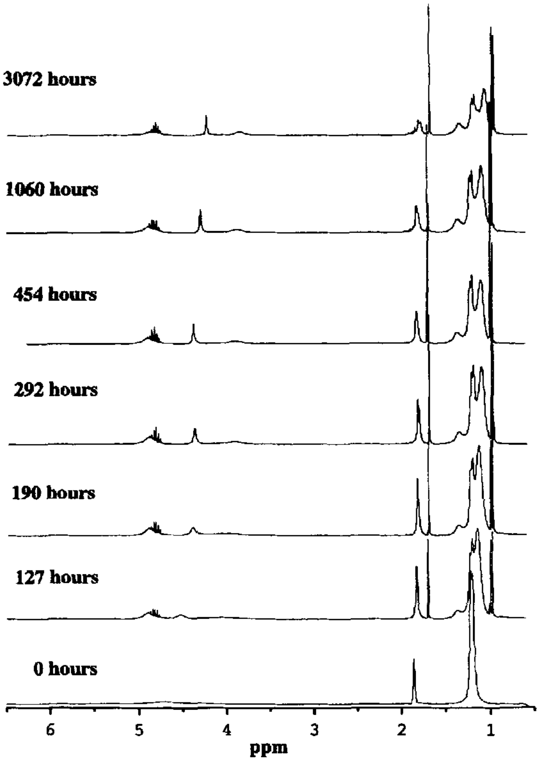


FIGURE 3 Proton NMR spectra of the reaction mixture of $Ti(OCHMe_2)_4$ + HOAc.

reaction continues (72 h), new peaks associated with free $HOCHMe_2$, $AcOCHMe_2$,[22] Ti-$OCHMe_2$, and Ti-OAc appear. The methine region has one well-defined septuplet and two broad methine resonances as well as the original methyl resonances. These peaks continue to grow and sharpen over several months until ultimately four types of methine protons, five types of methyl groups (two multiplets, associated with the HOAc and $OCHMe_2$ resonances) are produced. Based on integration of two of the major peaks, it has been determined that the majority of the reaction occurs within 72 h; however, subtle changes are still occurring for up to 2000 h. Understanding these changes should help elucidate some of the problems in the aging of PZT film solutions.[7b] Both the titanium and zirconium reactions are being monitored by ^1H, ^{13}C, ^{17}O (natural abundance) NMR over the same time frame to help in determining the lifetime of some of the intermediate products.

When $n = 1$ or 2, the ^1H NMR spectra of the crystalline material obtained from the titanium or zirconium and acetic acid reactions are very complex and difficult to interpret, unlike those reported by Sanchez.[20a] The ^1H NMR spectrum of the titanium crystalline compounds have as few as three types of methine protons ($n = 1$) or as many as seven types of methine resonances ($n = 2$). There appear to be two types of methyl resonances: one multiplet associated with the acetate methyl group and another multiplet associated with the diastereotopic methyls of the *iso*-propoxide ligands. Even the crystals of **1** in solution appear to undergo some form of dynamic behavior over time. During this period, the solution turns from a colorless solution to a deep blue color. This was found to occur when a solution of $Ti_6(OCMe_3)_{12}(OAc)_4O_4$ was irradiated with an Hg lamp for a few minutes.[20b] The color, which could be removed by exposure to oxygen, has been reported to arise from an intervalence Ti^{4+}–Ti^{3+} band.[20b] However, in the ^1H NMR spectrum, as the intensity of the color increases there is a decrease in one of the methyl resonances without any alteration in the methine region. There is no broadening at the half peak height of these resonances which is normally associated with paramagnetic compounds. The spectrum of the zirconium to HOAc reaction product is as complex as the titanium product, with up to six methine resonances observed. These compounds also demonstrate a blue discoloration over a prolonged period of time in solution.

The ^{13}C NMR spectra for these compounds are just as uninformative as the ^{1}H NMR spectra due to the large number of resonances observed. Therefore, we are currently investigating the natural abundance ^{17}O NMR spectra of these solutions. This technique is being developed and used to monitor the intermediate and final products produced. The initial spectrum obtained on the reaction mixture indicates that four major types of oxygen species are being generated (see Fig. 4). None of the peaks observed coincide with any of the starting material resonances. These peaks have been tentatively assigned based on reference data peaks.[24] The first peak at δ 33.8 ppm coincides with free $HOCHMe_2$ produced in this reaction. The other by-product of Eq. (2a) is *iso*-propylacetate, $CH_3C(O)OCHMe_2$. The second peak at δ 195.4 has been assigned to the $CH_3C(O)\mathbf{O}CHMe_2$ fraction of this product where the acetate oxygen ($CH_3C(\mathbf{O})OCHMe_2$) is present at δ 360.1. There is a shoulder present on this peak and has been attributed to the $\mathbf{O}CHMe_2$ ligand resonance. The peak is broadened due to the dynamic exchange of terminal and bridging $OCHMe_2$ ligands, which is also observed in the ^{1}H NMR spectrum. The resonance at δ 503.4 has been assigned as the Ti-$\mathbf{O}$Ac resonances. $Ti_6(OCHMe_2)_{12}(OAc)_4O_4$ crystals were produced from a similarly aged reaction mixture. Based on literature reports,[9,20] we expect to see the following reaction pathways (Eqs. (3)–(7), R = $CHMe_2$) for both series of compounds.

initial

$$6\,M(OR)_4 + 12\,HOAc \rightarrow M_6(OR)_{16}(OAc)_8 + 4\,HOAc + 8\,HOR \quad (3)$$

esterification

$$8\,HOR + 4\,HOAc \rightarrow 4\,ROAc + 4\,H_2O + 4\,HOR \quad (4)$$

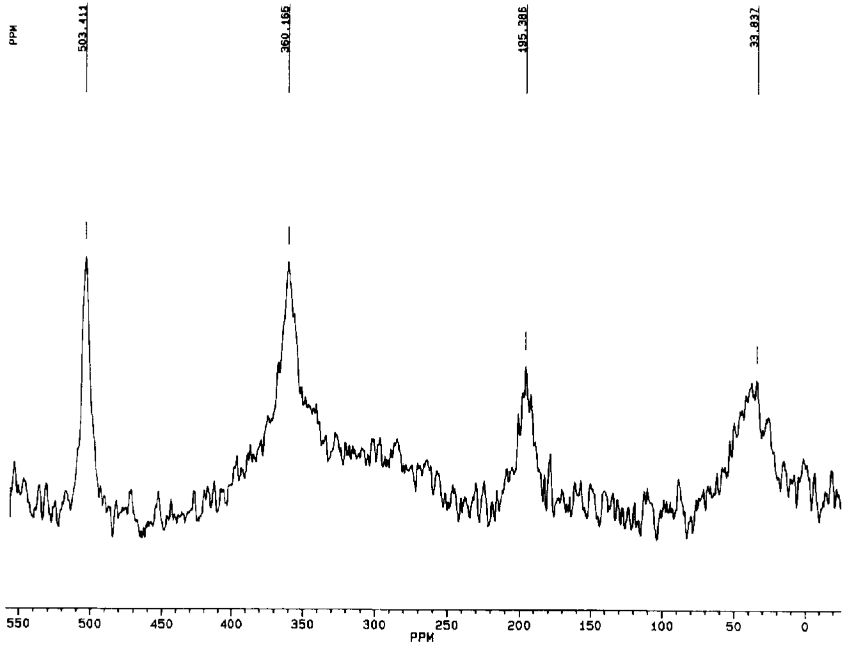


FIGURE 4 Oxygen-17 NMR spectrum of the reaction mixture of $Ti(OCHMe_2)_4$ + HOAc.

hydrolysis

$$M_6(OR)_{16}(OAc)_8 + 4\ H_2O \rightarrow M_6(OR)_{12}(OAc)_8(OH)_4 + 4\ HOR \quad (5)$$

oxolation

$$M_6(OR)_{12}(OAc)_8(OH)_4 \rightarrow M_6(OR)_8(OAc)_8(O)_4 + 4\ HOR \quad (6)$$

---

overall

$$2\ Ti_3(OR)_{12} + 12\ HOAc \rightarrow Ti_6(OR)_8(OAc)_8O_4 + 12\ ROH + 4\ ROAc \quad (7)$$

At this time we are monitoring the in-growth of products from M = Zr, Ti; $n = 1, 2$. Also, a series of experiments using enriched ^{17}O acetic acid have been initiated to elucidate the origin of the oxide.

1.2 Ti(OCHMe$_2$)$_4$/HOAc Precursor Conversion to the Ceramic Phase

The time-dependent NMR studies (Fig. 3) clearly indicate that the solution composition and precursor characteristics vary with time. To determine the importance of these variations on thin film properties, our initial film investigations have focused on studying the room temperature consolidation behavior of the as-deposited films. This should provide information on the nature of the monomer/oligomer aggregation processes which occur during deposition and drying.[25] Film consolidation was followed by ellipsometric measurements of film thickness and refractive index. Two types of coating solutions were prepared for spin-cast deposition. For the first solution, a sized aliquot of the reaction mixture was diluted in toluene; for the second coating solution, crystalline precursor **1** was dissolved in toluene. Both coating solutions were 0.25 M (Ti), and resulted in the preparation of uniform, transparent films with ~800 Å thickness, by spin-casting at 4000 rpm. Consolidation at room temperature was approximately 45% of the original thickness for films prepared from both solutions. This level of consolidation is greater than that previously observed for zirconia films prepared from acetyl acetone and acetate-based precursor systems,[25] and is most likely related to the lower solution concentration and the use of toluene as the solvent.

While we had originally expected to note differences in film consolidation behavior with changes in reaction time, perhaps the observed similarity for the two coating solutions is not unreasonable. The nuclearity of the precursor species increases for the longer reaction times, eventually to the point where crystallization of the hexameric complex **1** occurs[20a]; however, the general characteristics (i.e., accessibility of the alkoxy ligands) of the intermediates which lead to **1** are basically the same as **1**. Therefore, the susceptibility to ambient hydrolysis and the subsequent interaction during spin-cast deposition are unaffected. Hence, the resulting films should indeed be expected to display similar consolidation behavior.

TGA/DTA were used to study the weight loss and crystallization behavior of the neat reaction mixtures and dried powders. Longer reaction times, which produce species of higher nuclearity, resulted in increased weight loss at lower temperatures. This type of behavior has been noted previously for more highly condensed lead titanate precursors.[27] Surprisingly, the shift of the decomposition steps to lower temperatures results in a material characteristic that is more reminiscent of the starting parent alkoxide, $Ti(OCHMe_2)_4$ (major decomposition step ~150°C).

While only minor effects of precursor nuclearity on consolidation behavior were noted above, we plan further studies of other film properties, most notably studies of the relationship between nuclearity and crystallization. Since these *simple* reactions have proven to be very complex and yield novel products, we have undertaken the synthesis of compounds with the desired properties pre-determined by the ligand.

II. Increased Steric Bulk (Ref. 26)

Synthesis and Characterization of Adamantanol Group IV Derivatives

Due to the difficulties encountered in the characterization of the titanium and zirconium alkoxy acetate systems, the synthesis of a series of sterically hindering metal alkoxides was undertaken to determine if increased steric bulk would decrease the rate of hydrolysis by ambient water in the atmosphere. One ligand which was of interest due to its morphology is adamantan-1-ol[28] (AdamO-H, thermal ellipsoid drawing shown in Fig. 5). Since the chemical identity of the products of any binary or ternary alkoxide system consisting of Pb, Zr, and/or Ti would be more difficult to characterize than the single component systems, the initial studies focused on production of titanium and zirconium adamantanoxy derivatives individually. Formation of the lead alkoxides was initially omitted due to two reasons: (1) lead alkoxides have a tendency to polymerize[29] and (2) the carcinogenic nature of metallo-

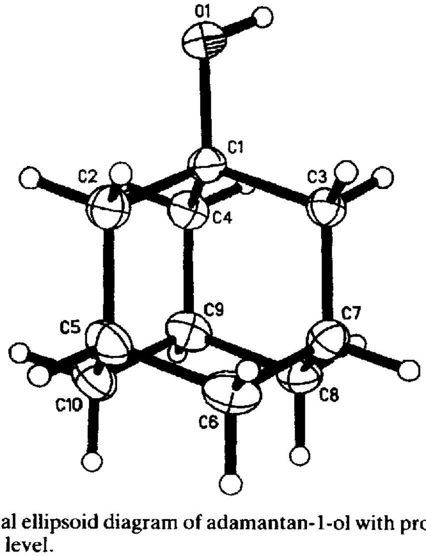
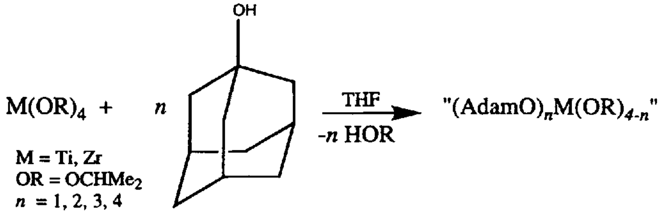


FIGURE 5 Thermal ellipsoid diagram of adamantan-1-ol with probability ellipsoids drawn at the 50% level.

organic lead compounds predicated postponing preparation of this precursor until the other reaction conditions had been optimized.

A series of reactions with varying stoichiometries (n = 1, 2, 3, 4) was undertaken which generated metal alkoxide compounds of systematically increasing steric bulk (Eq. (8)).



(8)

The procedure followed for synthesis of these compounds was a slight modification of a published procedure for formation of $(AdamO)_4Ti$.[30,31] This methodical replacement of $OCHMe_2$ with AdamO ligands was observed for the final product, both in solution and the solid state.

^1H and ^{13}C NMR indicated that for both the titanium and zirconium derivatives, an integral relationship exists between loss of *iso*-propoxide resonances and increase in the adamantanoxy resonances, until complete replacement has occurred. Based on the sharpness of the peaks in the ^1H NMR there appears to be little dynamic behavior associated with most of these compounds (at room temperature) indicating that the structure in the solid state should be consistent with that in solution. The zirconium adducts tend to exhibit broader peaks which would indicate some fluctionality in the solution state structure. However, since these compounds precipitate out of solution at slightly reduced temperatures, variable temperature NMR studies, which could have helped elucidate any dynamic behavior and therefore additional structural information, were not forthcoming.

The thermal behavior of the dried powders of these compounds was also investigated by TGA/DTA.[32] Figure 6 shows the TGA/DTA of the "$(AdamO)_nM(OCHMe_2)_{4-n}$" (M = Zr; n = 1–4) compounds under an atmosphere of oxygen. This was undertaken to obtain information on the transformation to the ceramic phase, since pyrolysis plays a key role in defining processing behavior,

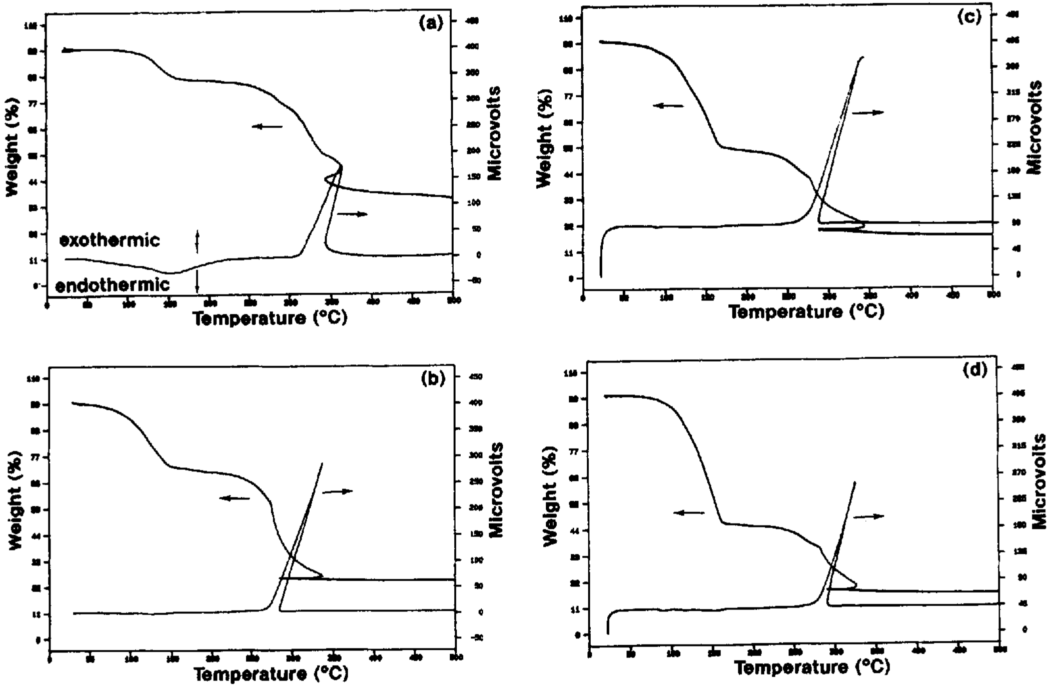
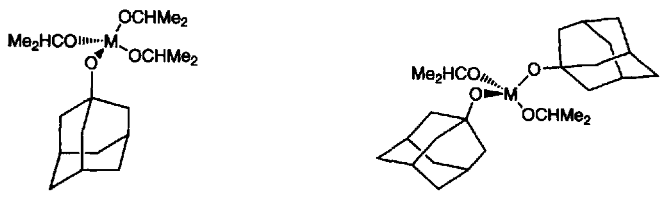


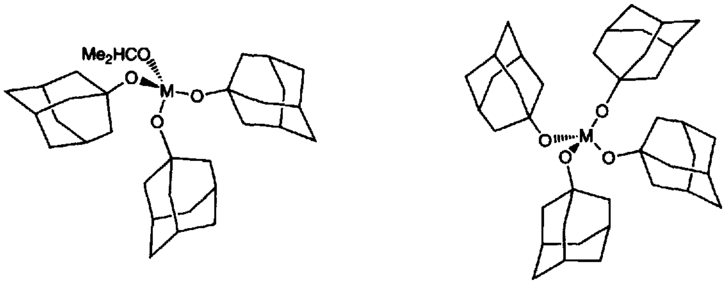
FIGURE 6 TGA/DTA spectra of: (a) "(AdamO)Zr(OCHMe$_2$)$_3$", (b) "(AdamO)$_2$Zr(OCHMe$_2$)$_2$", (c) "(AdamO)$_3$Zr(OCHMe$_2$ and (d) "(AdamO)$_4$Zr".

crystallization onset temperatures, and sintering temperatures. Under an argon atmosphere, "(AdamO)Zr($OCHMe_2$)$_3$" exhibits a decomposition step at ~325°C (see Fig. 6(a)). With increased adamantanol substitution, the weight loss is shifted to lower temperatures, although some contribution of the higher temperature decomposition steps may again be noted. Interestingly, this response mimics the conversion displayed by the extended time Ti to HOAc solution precursors; however, structural information on the AdamO compounds is required to completely understand the transformation behavior. Under a circumjacent atmosphere of argon, the TGA behavior of the zirconium compounds is similar to their behavior under oxygen; higher adamantanoxy substitution results in lower temperature decomposition steps of greater magnitude. The TGA spectra of the titanium analogs under argon exhibit essentially the same behavior; however, under oxygen their behavior is somewhat different. For these compounds, as the degree of substitution is increased, the lower temperature decomposition steps diminish, and essentially all of the weight loss occurs in the higher temperature decomposition step. In the DTA spectra of the adamantanoxide compounds for both titanium and zirconium, there is a large exotherm that occurs at the same temperature, regardless of the metal or degree of substitution by the adamantanol. The characteristic recoalescence peak observed in these compounds (Ti or Zr with oxygen as the circumjacent gas) has been routinely observed in our lab for crystalline titanium and zirconium alkoxide materials under an oxygen atmosphere.[33]

Currently, X-ray crystallographic studies of the solid state structures of selected "$(AdamO)_nM(OR)_{4-n}$" (M = Ti, Zr; R = $CHMe_2$) compounds are under investigation. This, coupled with molecular weight determinations, will elucidate the solid state structure versus the solution state structure. Drawings in Fig. 7 show the basic substitution processes undergone in Eq. (8) to produce the proposed "$(AdamO)_nM(OR)_{4-n}$" products. There are only two reports of transition metal adamantanoxide structures in the literature: $(AdamO)_4Mo(NHMe_2)$ [31] and $[(AdamO)Zn(CH_2SiMe_3)]_4$.[34] We assume the higher substituted titanium and zirconium compounds (n = 3 or 4) are mononuclear, as reported above for the highly substituted molybdenum compound. This idea is furthered by literature reports on monomeric titanium compounds which



"(AdamO)M(OCHMe$_2$)$_3$" "(AdamO)$_2$M(OCHMe$_2$)$_2$"



"(AdamO)$_3$M(OCHMe$_2$)" "(AdamO)$_4$M"

FIGURE 7 Substitution of "M(OCHMe$_2$)$_4$" (M = Ti, Zr) by AdamO-H.

possess large aryl alkoxide co-ligands,[35] and simple molecular models which indicate that a large steric interaction between adamantanoxy ligands occurs if the nuclearity is greater than one.

The lower substituted titanium compounds are probably oligomeric based on previous structural information for titanium alkyl alkoxides.[36] Furthermore, titanium has a tendency to coordinately saturate its binding sphere,[36,37] unless a large number of sterically hindering ligands are used.[35] Therefore, it is probable that the central core consists of inter-linked titanium *iso*-propoxide moieties which are protected by an outer sphere of adamantanol ligands. The potential structure of "(AdamO)Ti(OCHMe$_2$)$_3$" is illustrated in Fig. 8(a). The adamantanoxy ligands would sweep out a very large area relative to the *iso*-propoxides which would not allow for attack by ambient humidity.

The lower substituted zirconium complexes gel during deposition, as might be deduced from the structure of zirconium *iso*-propoxide. This compound is known to be a dimeric complex,

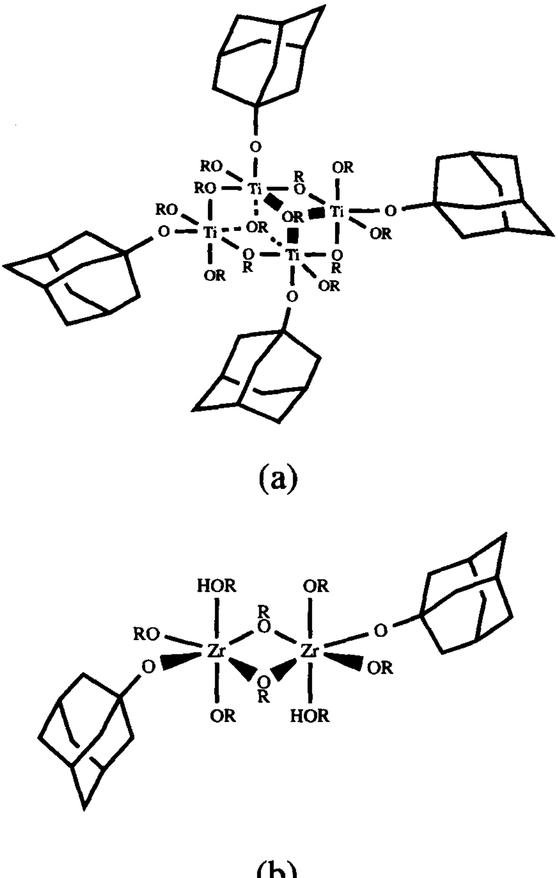
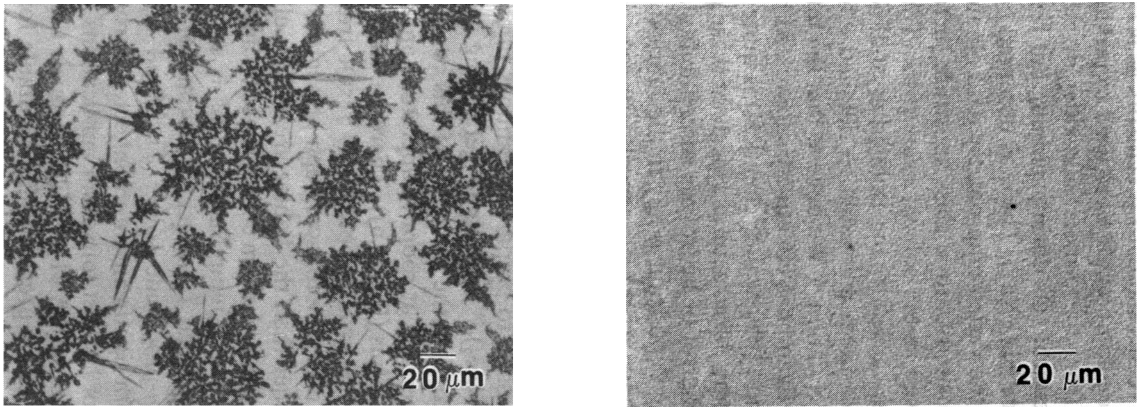


FIGURE 8 Possible structure for: (a) "(AdamO)Ti(OR)$_3$"; (b) "(AdamO)Zr(OR)$_3$" (R = CHMe$_2$).

[Zr(OCHMe$_2$)$_4$·HOCHMe$_2$]$_2$.[38] In Eq. (8) with $n = 1$, a simple substitution could occur to form the empirical compound "(AdamO)Zr(OCHMe$_2$)$_3$," without disruption of the dimer (Fig. 8(b)). Therefore, this compound would retain the easily exchanged alcohols associated with the starting material and would still be readily susceptible to gelation due to ambient hydrolysis. However, with this increase in steric bulk there should be some reduction in hydrolysis sensitivity versus standard precursors as is observed.

The adamantanoxide compounds were used to produce films.[39] The films deposited from these metal alkoxides do not produce either physical or chemical gels during spinning but tend to form crystalline clusters (see Fig. 9(a)). This was observed both by optical microscopy and the varied ellipsometry data obtained. For a solution droplet deposited onto a glass substrate, actual crystal growth can be observed as the solvent evaporates. The non-uniformity of these films, caused by the isolated crystalline environments, does not make them amenable to detailed ellipsometric investigations of consolidation.[40] We believe that the introduction of the adamantanoxy ligand has effectively suppressed hydrolysis. The lack of any gelation (physical or chemical) is quite surprising and may be explained by the structural aspects of these precursors (*vide supra*). While control of hydrolysis susceptibility and oligomer interaction during deposition is key in the fabrication of uniform thin films which have acceptable consolidation characteristics, the monomeric nature of the higher substituted precursors and their insensitivity to hydrolysis make them unsuitable as thin film precursors. Since the precursors simply re-crystallized during deposition, it was not possible to prepare continuous films.[41]

"(AdamO)Zr(OCHMe$_2$)$_3$" appears to gel during spin casting, which is probably related to the structure of this compound (*vide supra*). The films generated at room temperature are as uniform as the other precursor films (Fig. 9(b)). There are small variations in thickness of the films, which potentially result from a phase separation process.[42] In the photomicrograph presented, the darker areas are slightly thinner than the lighter areas. The ellipsometry data (Fig. 10) indicates that the film consolidates by approximately 30% after 2 hours at room temperature. This is comparable to zirconia thin films prepared from acetyl acetone or acetic acid modified zirconium *n*-propoxide sols.[25] The fired films appear granular in nature, with significant interconnected porosity. Structures of this type are of interest for sensor applications.[43] It is thus possible to control the nature of the film through the extent of ligand substitution, thereby preparing films suitable for a variety of different applications.



A. Film prepared from a 0.15M "$(AdamO)_2Ti(OCHMe_2)_2$" in toluene. The lighter contour is the substrate.

B. Film prepared from 0.15M "$(AdamO)Zr(OCHMe_2)_3$" in toluene.

FIGURE 9 Thin films of selected adamantan-1-ol compounds spin-cast deposited onto a silicon substrate.

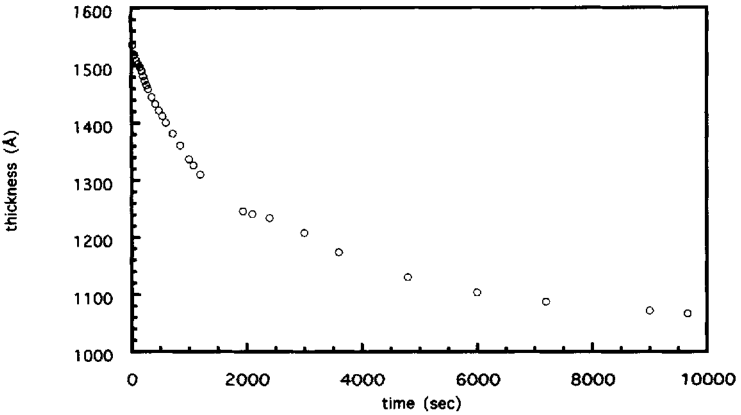


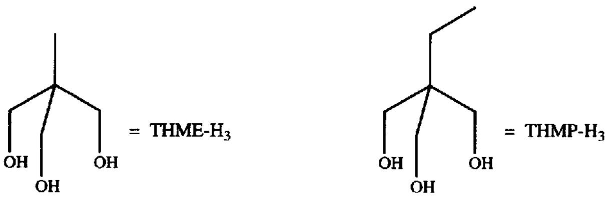
FIGURE 10 Plot of thickness (Å) versus time (sec) for "(AdamO)Zr(OCHMe$_2$)$_3$".

III. Increased Binding Modes

Synthesis and Characterization of Tridentate Alkoxide Complexes

The admanatanol ligands effectively suppressed the hydrolysis susceptibility of the Ti and Zr compounds; however, some form of gelation process (chemical or physical) is required for the formation of continuous, uniform films. Therefore, it was necessary to investigate precursors with sterically less demanding ligands that do not crystallize upon deposition. To accomplish this and to control the nuclearity of starting materials, we have begun the investigation of tridentate alkyl alkoxide ligands.

Tridentate alkyl alkoxide ligands were chosen due to their similarity to standard starting materials, the variety of binding modes possible, the stability of both the ligand and the products formed, the variance in steric bulk available, the solubility, and the ease of derivatization. Furthermore, there is a surprising paucity of tridentate alkoxide structures reported in the literature.[44,45] The tridentate ligands being investigated include: 1,1,1-tris(hydroxymethyl)ethane (THME-H_3, Aldrich), 1,1,1-tris(hydroxymethyl)propane (THMP-H_3, Alfa), 1,3,5-cyclohexanetriol (CYHT-H_3, Aldrich), and 2,2-bis(hydroxymethyl)proprionic acid (BHMP-H_3, Aldrich) (see Fig. 11).



1,1,1-Tris(hydroxymethyl)ethane

1,1,1- Tris(hydroxymethyl)propane

1,3,5-Cyclohexanetriol

2,2-Bis(hydroxymethyl)proprionic Acid

FIGURE 11 Abbreviations for tridentate ligands investigated.

The first systems studied were the 1,1,1-tris(hydroxymethyl)ethane ($THME\text{-}H_3$) and 1,1,1-tris(hydroxymethyl)propane ($THMP\text{-}H_3$) tridentate ligands. These alkoxides fit the initial criteria of being easily obtained, stable, and alkyl alkoxides. Other desirable characteristics are the ease of derivatization,[46] as well as the variety of binding modes possible with these ligands. For both metals and $THME\text{-}H_3$, a 1 to 1 reaction stoichiometry resulted in the isolation of insoluble white powders. These powders were not soluble in any of a variety of solvents and temperatures evaluated, and therefore were not further characterized. When the stoichiometry was increased and optimized at a ratio of 1 to 2, crystalline material was obtained for both metal alkoxides (Eq. (9) and Eq. (10)).

$$2\ \mathrm{THME\text{-}H_3} + 4\ \mathrm{Ti(OCHMe_2)_4}$$

$$\xrightarrow[-6\ \mathrm{HOCHMe_2}]{\text{toluene/THF}} \mathrm{(THME)_2Ti_4(OCHMe_2)_{10}} \qquad (9)$$

$$2\ \text{THME-H}_3 + 2\ [\text{Zr}(\text{OCHMe}_2)_4\cdot\text{HOCHMe}_2]_2 \xrightarrow[-10\ \text{HOCHMe}_2]{\text{toluene/THF, reflux temp.}} (\text{THME})_2\text{Zr}_4(\text{OCHMe}_2)_{10} \quad (10)$$

The resulting product of Eq. (9) was identified as $(\text{THME})_2\text{Ti}_4(\text{OCHMe}_2)_{10}$, **3**. A thermal ellipsoid drawing of the solved X-ray crystallographic study is shown in Fig. 12. This is a typical fused M_3O_{12} structure commonly observed for titanium alkyl alkoxides.[36] **3** is thermally unstable. Warming a toluene solution of **3** above 45°C results in the formation of a white precipitate, which is no longer soluble in a wide variety of solvents. The solubility limit of **3** is approximately 0.07M in toluene, and it is stable in solution for up to three months. The product of Eq. (10) was also identified by X-ray crystallographic studies as $(\text{THME})_2\text{Zr}_4(\text{OCHMe}_2)_{10}$, **4**, and a thermal ellipsoid representation is shown in Fig. 13. **4** is significantly different from **3** in that

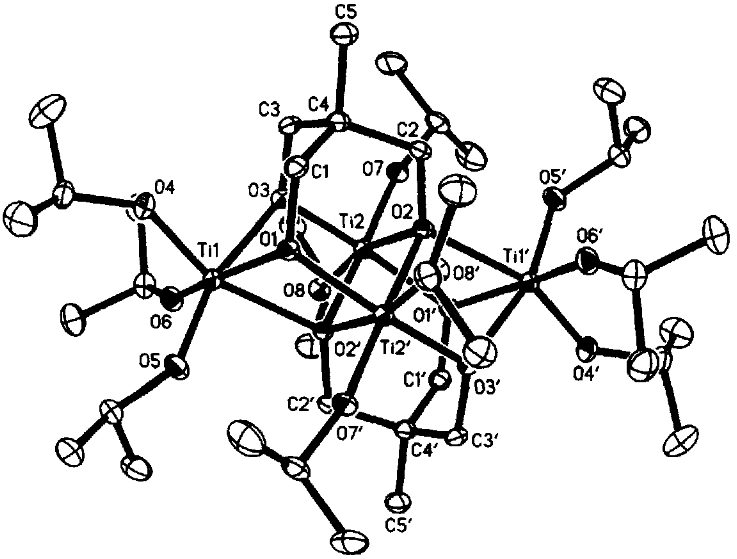


FIGURE 12 Thermal ellipsoid diagram of $(\text{THME})_2\text{Ti}_4(\text{OCHMe}_2)_{10}$, **3**, with probability ellipsoids drawn at the 50% level.

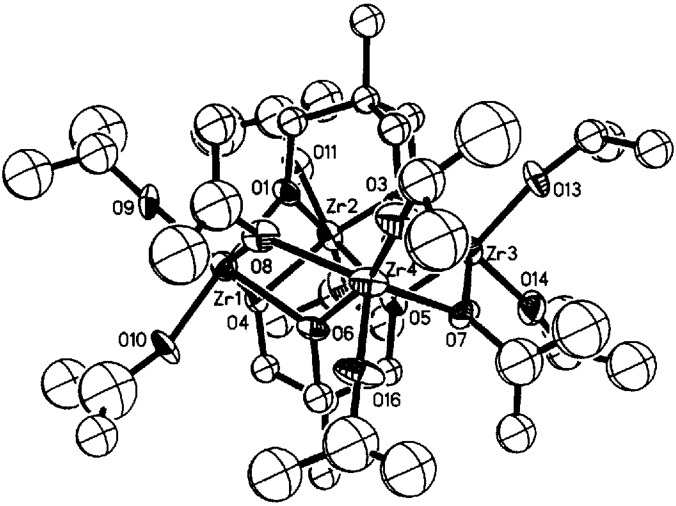


FIGURE 13 Thermal ellipsoid diagram of $(THME)_2Zr_4(OCHMe_2)_{10}$, **4**, with probability ellipsoids drawn at the 50% level.

there are bridging *iso*-propoxide ligands and no triply bridging oxygen atoms. Details of the synthesis, metrical data, and reactivity of both of these compounds will be reported at a later date.^{47}

After the determination of the appropriate stoichiometry for Eqs. (9) and (10), analogous reactions utilizing $THMP\text{-}H_3$ were undertaken (Eqs. (11) and (12)).

$$2\ THMP\text{-}H_3 + 4\ Ti(OCHMe_2)_4 \xrightarrow[-6\ HOCHMe_2]{\text{toluene/THF}} (THMP)_2Ti_4(OCHMe_2)_{10} \quad (11)$$

$$2\ THMP\text{-}H_3 + 2\ [Zr(OCHMe_2)_4\cdot HOCHMe]_2 \xrightarrow[-10\ HOCHMe_2]{\substack{\text{toluene/THF}\\ \text{reflux temp.}}} (THMP)_2Zr_4(OCHMe_2)_{10} \quad (12)$$

The isolated product from Eq. (11) proved to be $(THMP)_2Ti_4(OCHMe_2)_{10}$, **5** (Fig. 14 is a thermal ellipsoid representation of

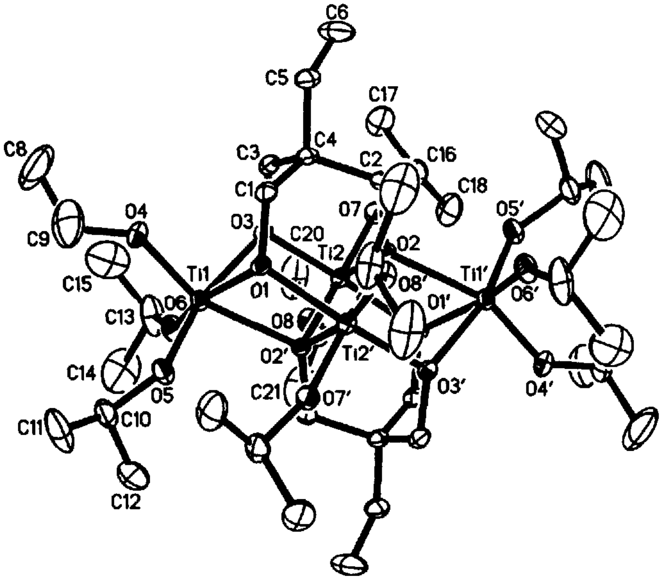


FIGURE 14 Thermal ellipsoid diagram of $(THMP)_2Ti_4(OCHMe_2)_{10}$, **5**, with probability ellipsoids drawn at the 50% level.

the results of the single crystal X-ray crystallographic study). Not surprisingly, the structure is identical to that of **3**; however, the characteristics of **5** are slightly different than that of **3**. The reaction mixture of Eq. (11) can be slightly warmed without any precipitate forming. Increased heating results in the formation of an insoluble white precipitate upon cooling, coupled with the formation of crystals which possess the same NMR spectrum as the unwarmed solution. The zirconium analog of this reaction also appears to form an analog of **4**. The proposed formula is $(THMP)_2Zr_4(OCHMe_2)_{10}$ (a single crystal X-ray study is underway). The THMP derivatives of both metals appear to possess increased solubility and stability in solution. All of these compounds (**3**–**5**) appear to be stable in solution for up to three months in solution.

TGA/DTA experiments[32] on **3**, **4** and the analogous starting materials $Ti(OCHMe_2)_4$, **6**, and $[Zr(OCHMe_2)_4 \cdot HOCHMe_2]_2$, **7** were undertaken. The spectra of these compounds are shown in Fig. 15.[23] Not surprisingly, the TGA/DTA spectra of **3** and **4** share

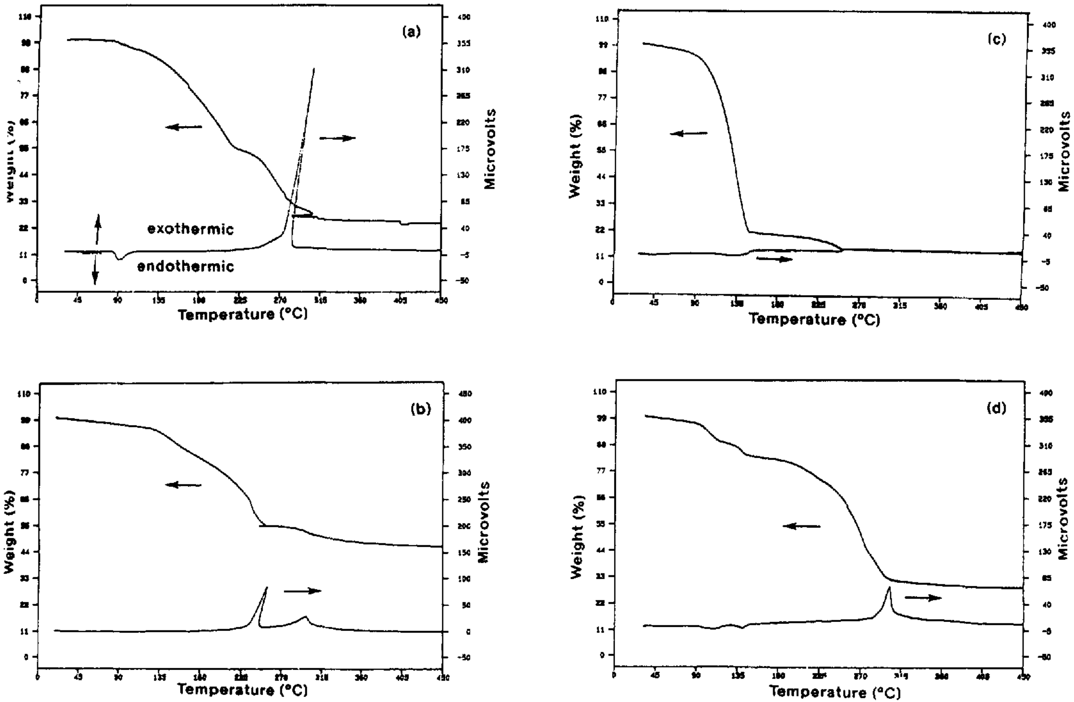


FIGURE 15 TGA/DTA spectra of: (a) $(THME)_2Ti_4(OCHMe_2)_{10}$, **3**, (b) $(THME)_2Zr_4(OCHME_2)_{10}$, **4**, (c) $Ti(OCHMe_2)_4$, **6**, and (d) $[Zr(OCHMe_2)_4 \cdot HOCHMe_2]_2$, **7**.

some striking similarities. Both spectra display a large weight loss recorded in the TGA without corresponding large thermal events observed in the DTA. For **3** the weight loss occurs up to ~200°C, whereas for **4** the weight loss is observed up to ~150°C, similar to that observed in **7**. In the TGA of both compounds there is then observed a very large exothermic recoalescence peak (275°C, **3**; 230°C, **4**) with a corresponding 20–30% weight loss recorded in the TGA. These decomposition steps are assumed to be the synchronous loss of the organic fraction of the ligands. It is of interest to note that the exothermic peak of **3** is significantly larger than the peak observed in the thermal treatment of **4**. Furthermore, neither of the starting materials record this large exotherm. Thus, while the tridentate compounds still retain some similarity to the starting compounds, they display large recoalescence peaks not observed for the parent alkoxides. Such recoalescence peaks, indicative of highly exothermic behavior, have been noted previously in thermal analysis studies of ethoxide-derived lithium niobate gels.[48]

After the large recoalescence peaks in the spectra of **3** there are no more thermal events or weight losses recorded. Since no more events are recorded, this large thermal event is most likely the additive feature of organic pyrolysis and the transformation of the remaining material to the ceramic oxide, TiO_2. For **4**, around 300°C there appears a second recoalescence peak which coincides with the recoalescence peak in **7**. For **4**, this peak may again represent final organic pyrolysis and the conversion of the remaining material to the ceramic oxide, ZrO_2. The TGA/DTA data indicates that THME ligated compounds **3** and **4** behave much differently in the solid state than **6** and **7**, respectively. The recoalescence peaks may be an indication of highly ordered powders wherein the organic fraction burns off concurrently. This would explain why **3**, **4**, and **7** all exhibit exotherms whereas **6** (a liquid) does not. Based on the comparison of the TGA/DTA of **3** and **4** there appears to be some similar characteristic carryover.

^1H NMR spectra of **3** and **4** show that the solid state structural integrity is maintained in solution. For both of these compounds there is evidence for some minor dynamic processes occurring, but this is hard to explicate since at lower temperatures both the zirconium and the titanium compounds readily crystallize out of solution. At higher temperatures (>35°C) 3 undergoes a rearrangement. This produces a white insoluble powder and the ^1H NMR of the reaction products indicates $Ti(OCHMe_2)_4$ has been re-formed. 4 also undergoes a dynamic process at elevated temperatures; however, it is readily apparent that the central THME binding modes are maintained at this temperature by the consistency of the methyl resonance of the THME ligand. What is assumed to be occurring is exchange of the terminal $OCHMe_2$ and μ-$OCHMe_2$ bridging ligands. After cooling this solution back to room temperature, an identical ^1H NMR spectrum is obtained as previously recorded at ambient temperature.

Film generation from solutions of 3 and 4 was undertaken in an analogous manner as reported earlier.[39] The solutions were made up in toluene at a concentration of 0.07 M due to the extremely low solubility of 3. As before, film results were obtained only on films heat treated under an oxygen atmosphere. These films were also compared to standard starting materials, 6 and 7. Due to the increased steric bulk and the closely bound central M_4O_4 core, hydrolysis was significantly reduced; however, it was not eliminated. All of the films produced had extensive macroscopic cracking. Films prepared from 6 and 7 instantly became opaque upon the initiation of spinning, an indication of hydrolysis. Film fabrication from solutions of 3 and 4 took up to 5 sec to form a cloudy surface, which suggests that the hydrolysis susceptibility, while not eliminated, was dramatically reduced versus the parent alkoxides, 6 and 7.

The films of 3 and 4, as compared to 6 and 7, yielded some interesting results in the fired films topology. 6 exhibited large pores which were significantly reduced after firing; however, the film from the solution of 3 had become very granular in nature. The films generated from 4 appeared relatively unaffected by firing. Nonetheless, films prepared from a solution of 4 showed significantly reduced cracking and less reactivity with ambient humidity than 7. While these results are of interest, the preparation of continuous transparent films requires precursors with still less susceptibility to ambient humidity.

Initial investigations into the tridentate systems, 1,3,5-cyclohexanetriol (CYHT-H_3) and 2,2-bis(hydroxymethyl)proprionic acid (BHMP-H_3), have not met with as much success as reported for

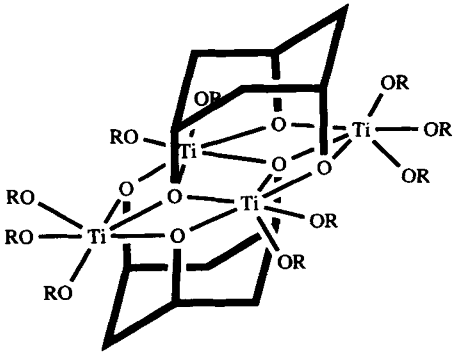


FIGURE 16 Possible structure for "$(CYHT)_2Ti_4(OR)_{10}$" (R = $CHMe_2$).

the THME and THMP systems. CYHT was chosen due to its similarity to the THME ligand but with a different distribution of steric bulk. In the CYHT-H_3 system, analogous reactions to Eq. (9) were undertaken. Once again, the 1 to 1 reaction produced an insoluble product. The 1:2 reaction product (Eq. (13)) was isolated as a crystalline white solid.

$$2\ \text{CYHT-}H_3 + 4\ Ti(OCHMe_2)_4 \xrightarrow[-6\ HOCHMe_2]{\text{toluene/THF}} (CYHT)_2Ti_4(OCHMe_2)_{10} \qquad (13)$$

The ^1H and ^{13}C NMR spectra of this powder are similar to that observed for **3** and **4**. Based on this similarity, and since other alkyl alkoxide titanium compounds have been shown to adopt the M_3O_{12} structure, we assume the reaction product of Eq. (13) will be found to be similar (i.e., $(CYHT)_2Ti_4(OCHMe_2)_{10}$, **12**, Fig. 16). However, at this time, all attempts to crystallize this compound have resulted in microcrystalline powder.

The BHMP-H_3 ligand (Fig. 11) is of interest due to the variable binding sites available. In standard sol-gel preparations for PZT materials, metallo-alkoxides are frequently reacted with acetic acid resulting in mixed alkoxy acetate compounds.[6] Products from the reaction of BHMP-H_3 with **7** and **8** may mimic some of the structural types generated in the initial PZT processes. Preliminary studies using this ligand are underway. The low solubility of the BHMP ligand in organic solvents appears to be the largest deterrent to reactivity.

SUMMARY

We have begun to investigate the possibility of controlling ceramic film processing behavior through the use of modifying ligands. The main focus of our studies has been to add sterically hindering or multidentate ligands to Group IV metals. Based on the compounds generated with the adamantanoxy ligands, we have demonstrated that hydrolysis by ambient humidity can be completely removed in association with these metal alkoxides. Unfortunately, these precursors crystallized instead of displaying the expected gelation behavior required to form uniform films. The tridentate ligands investigated indicate that co-ligands can be used to dictate the nuclearity of the smaller clusters, control hydrolysis by circumjacent water, and alter the microstructure of the resulting films. From the tridentate ligands investigated, there is observed a trend of the simple metal alkoxides to form tetranuclear compounds. Combining the adamantanol result with the tridentate ligands, we are undertaking the generation of large sterically demanding tridentate ligands. This should result in increased nuclearity with decreased hydrolysis.

Studies of the precursors typically generated have yielded some new and interesting results. First, it is possible to obtain ^{17}O NMR spectra on complex non-enriched compounds within a reasonable amount of time. This will be useful in identifying oxygen environments as soon as a data base is established. Even though Eq. (1) proceeds quite slowly, a large majority of the reaction has occurred in the first three days and we have begun to elucidate some of the compounds (**1** and **2**) formed in these reactions. These compounds appear to be much larger than anticipated with an oxide formed in the process.

While we have begun to develop an understanding of the chemistry of the precursor solutions, as well as some of the effects ligand type and precursor structure can have on the consolidation of crystalline ceramic thin films, a significant area of thin film processing remains to be developed. The important relationships between precursor structure, the intermediate range order which results from precursor aggregation during deposition, and the subsequent structural rearrangements which lead to crystal nucleation remain to be explored. While effects of structural variations on crystal nucleation and thin film microstructure have been noted,[49] it is difficult to study these relationships due to the inherent problems associated with the analysis of amorphous materials. The variations in material composition which accompany organic pyrolysis and dehydroxylation also complicate the analysis. These areas necessitate investigation because of the immense technological impact controlled ceramic microstructure will have on a large number of applications.

Acknowledgments

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were measured by ellipsometry (Gaertner L116-C). A topological surface picture (1000 ×) was then obtained by optical microscopy. From the same solution, two more films were generated under identical conditions. Film thickness and refractive index were obtained on these films and they were then fired under different circumjacent gases (O_2 or Ar). These films were heated at 10°C per min to 650°C and then fired at this temperature for 10 min. Thickness and refractive index data were once again obtained to determine densification. A photomicrograph (1000 ×) was also acquired to record any visual alterations in the surface microstructure.

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