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13. ABSTRACT (Maximum 200 words)

We have studied ester elimination in a number of model systems to determine the criteria which promote or inhibit such reactions. The model systems generally involve metal centers which possess NMR active nuclei such as ²⁹Si, ¹¹⁹Sn, ¹¹⁷Sn and ²⁰⁷Pb. In these systems, we have conducted a number of 170 labeling experiments which reveal that ester elimination is probably an associative process that requires electropositive metal alkoxide centers, accessible coordination sites at the metal centers, dangling carboxylate ligands and which is promoted by non-coordinating solvents and inhibited by coordinating solvents. In a heterobimetallic systems, the reaction between Sn(O-t-Bu)₄ and Pb(OAc)₄ results in formation of a metal oxo cluster in the presence of toluene. These metal oxo clusters retain their structure in solution as determined by multinuclear NMR spectroscopy for PbSn₂₀(O-t-Bu)₄(OAc)₄. As a result of this understanding gained from these model reactions, we are now in a position to investigate the formation of metal oxide materials using these clusters.

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Cover Page

Final Report for Air Force Office of Scientific Research

June 1996

**Hydrolysis and Condensation of Tin(IV) Alkoxide
Compounds: The Control of Structural Evolution**

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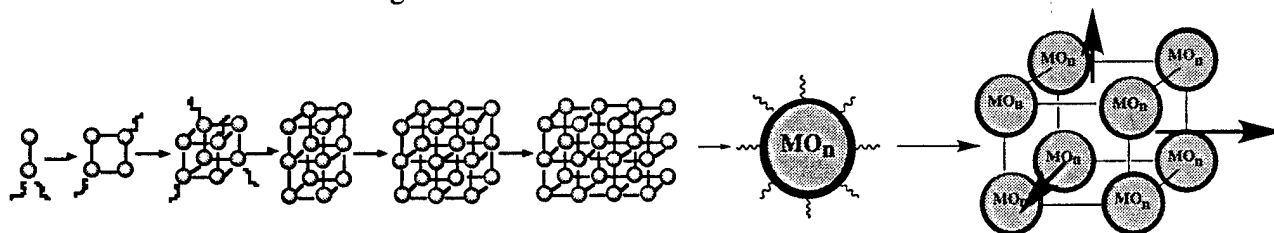
Air Force Grant Number: F 49620-93-1-0197DEF

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2. Objective:

To develop an understanding of how to control the evolution of microstructure during the formation of inorganic thin films.

We are interested in developing a fundamental understanding of how to control the evolution of microstructure in metal oxide materials. Metal oxide materials have a wide range of properties and therefore applications such as sensors, fuel cells, electronic devices (e.g. ferroelectric DRAMs), separation membranes. The control of microstructure including pore structure, density, composition, stoichiometry and crystallinity in the formation of films and bulk oxides on various substrates (dense or porous) is crucial to obtain the desired properties from these materials. Our strategy is to prepare molecular metal-oxo clusters in a systemic fashion from metal organic precursors. These clusters can then be used as molecular building blocks and as precursors themselves to assemble inorganic films or powders. These clusters could be assembled by specific polymerization reactions to link them in 1-, 2- or 3- dimensions to control the evolution of microstructure as shown below. Alternatively, where they have a particular internal structure, they are likely to influence the phase evolution when these clusters are used as precursors themselves for the formation of dense inorganic materials.

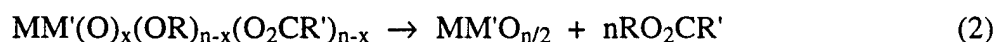


Potential benefits of a molecular building block approach to materials over conventional methods:

- Controlled microstructure, composition and homogeneity.
- New non-equilibrium (metastable or kinetically controlled) crystal phases may be formed.
- Potential for control over crystallization based on internal cluster structure.
- Possibility to assemble clusters in a well controlled fashion in 1, 2 or 3 dimensions.
- Anisotropic structures.
- Controlled pore structure amorphous materials possible.
- Possibility to prepare nanoclusters at the interface between molecules and materials.
- Better control over size and size distribution of clusters than existing surfactant-based methods.
- Test properties derived from quantum confinement.

3. Status of Effort:

Conventional hydrolytic routes to non-silicate metal oxide materials are often thwarted by the lack of control over hydrolysis and condensation rates in these systems. As an alternative to hydrolysis and condensation of metal alkoxide compounds we are exploring a strategy which involves ester elimination reactions between metal alkoxide and metal carboxylate compounds. In principle, this reaction can lead to the complete elimination of the organic supporting ligands to produce high purity materials and is also likely to provide the opportunity to isolate and identify intermediates which may allow for separate assembly of metal-oxo cluster intermediates, see equations 1 and 2.



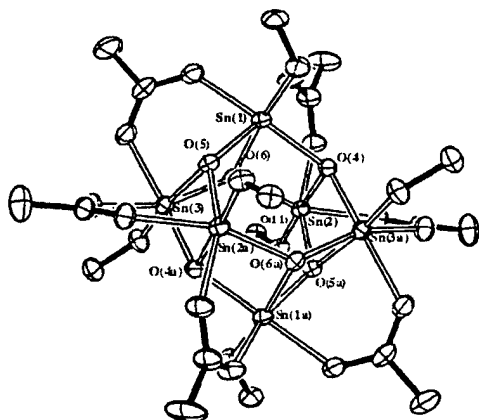
Thus far we have demonstrated that a series of metal oxo cluster building blocks can be prepared by ester elimination between metal alkoxides and metal carboxylates with the following features:

- homomultimetallic oxo clusters
- mixed valence homomultimetallic oxo clusters
- heteromultimetallic oxo clusters

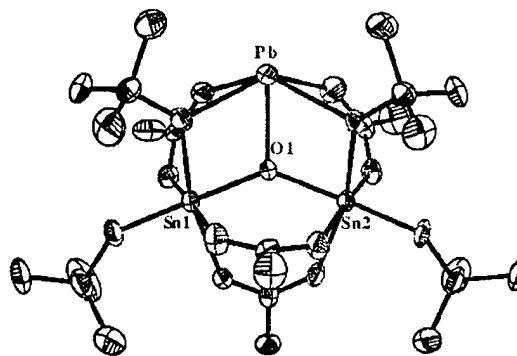
This fulfills the first objectives of this proposed research plan to make tin oxo clusters as model species which can be used as building blocks to controlled microstructure films.

4. Accomplishments

We have studied ester elimination in a number of model systems to determine the criteria which promote or inhibit such reactions. The model systems generally involve metal centers which possess NMR active nuclei such as ^{29}Si , 119 , ^{117}Sn and ^{207}Pb . In these systems, we have conducted a number of ^{17}O labeling experiments which reveal that ester elimination is probably an associative process that requires electropositive metal alkoxide centers, accessible coordination sites at the metal centers, dangling carboxylate ligands and which is promoted by non-coordinating solvents and inhibited by coordinating solvents. In a heterobimetallic system, the reaction between $\text{Sn}(\text{O}-t\text{-Bu})_4$ and $\text{Pb}(\text{OAc})_4$ results in formation of a metal oxo cluster in the presence of toluene. These metal oxo clusters retain their structure in solution as determined by multinuclear NMR spectroscopy for $\text{PbSn}_2\text{O}(\text{O}-t\text{-Bu})_4(\text{OAc})_4$. As a result of this understanding gained from these model reactions, we are now in a position to investigate the formation of metal oxide materials using these clusters.



$\text{Sn}_6\text{O}_6(\text{O}-t\text{-Bu})_6(\text{OAc})_6$



$\text{PbSn}_2\text{O}(\text{O}-t\text{-Bu})_4(\text{OAc})_4$

These cluster precursors are being converted into inorganic materials via liquid phase condensation reactions and via gas-solid reactions using Aerosol-Assisted Chemical Vapor Deposition (AACVD). Condensation reactions involve further ester elimination or the addition of bifunctional reagents such as dicarboxylic acids to determine if it is possible to link individual clusters and control the sizes of the linked clusters and examine the influence on the properties of the materials being formed. CVD with aerosol-assisted precursor delivery is a method which permits delivery of unusually high molecular weight clusters to surfaces to accomplish film deposition. This allows us to examine the influence of cluster structure on the nature of the films formed. For example, $\text{Sn}_6\text{O}_6(\text{O}-t\text{-Bu})_6(\text{OAc})_6$ possesses all the structural features of cassiterite phase SnO_2 (6-coordinate Sn and 3-coordinate oxo groups) and can be converted to oriented SnO_2 films at low temperatures by AACVD.

We have spent the last period of this grant investigating the ester elimination reactions between group 2 metal carboxylates and Group 4 metal alkoxides in an attempt to develop low temperature methods to prepare perovskite phase mixed metal oxides such as BaTiO_3 films which might be

suitable for applications in devices where ferroelectric, pyroelectric or piezoelectric properties are required.

Significant results from AFOSR-funded research:

- Developed a strategy to prepare metal oxo clusters in a systemic fashion.
- Understand some of the mechanistic details of ester elimination.
- Shown the method is applicable to a wide range of metal oxides
- Patent application was filed on the deposition of ferroelectric thin films e.g. BaTiO₃. Recently this US patent application was filed in a number of foreign countries also.
- Demonstrated that highly oriented metal oxide films can be reproducibly deposited on amorphous substrates. We believe we can control crystallinity and orientation based on the precursor structure rather than the substrate structure.

5. Personnel Supported:

Principal Investigator:	Prof. Mark J. Hampden-Smith
Post-doctoral Associates:	Dr. James Caruso Dr. Klaus Kunze
Graduate Students:	Adrian Groenendyk Pat Fleig

6. Publications:

- "Chemical Aspects of Solution Routes to Perovskite phase Mixed Metal Oxides from Metal-Organic Precursors." C.D. Chandler, C. Roger and M.J. Hampden-Smith, *Chem. Rev.*, **93**, 1205, 1993.
- "Solvent-Dependent Ester Elimination and Ligand Exchange Reactions between Trimethylsilyl Acetate and Tin (IV) Tetra-*tert*-butoxide." James Caruso, Christophe Roger, Fritz Schwertfeger, Mark Hampden-Smith, Arnold Rheingold and Glenn Yap. *Inorg. Chem.*, **34**, 449-453, 1995.
- "Ester Elimination Versus Ligand Exchange: The Role Of The Solvent In Tin-Oxo Cluster-Building Reactions." James Caruso, Mark J. Hampden-Smith, Arnold L. Rheingold, and Glenn Yap, *J. Chem. Soc. Commun.*, **2**, 157-158, 1995.
- "Structural Investigation of Tin(IV) Alkoxide Compounds, Part II. Solution Structural Characterization of [Sn(O-*i*-Bu)₄•HO-*i*-Bu]₂." Clive D. Chandler, James Caruso, Mark J. Hampden-Smith and Arnold L. Rheingold, *Polyhedron*, **14**(17-18), 2491-2497, 1995.
- "Solvent Dependent Ester Elimination Reactions in the Preparation of Mixed-Metal Oxo Clusters: The Synthesis of PbSn₂(μ³-O)(O-*t*-Bu)₄(OAc)₄." James Caruso, Mark J. Hampden-Smith and Eileen Duesler, *J. Chem. Soc., Chem. Commun.*, 1041-1042, 1995.
- "The Kinetics of Alcohol-Alkoxide Exchange Between Sn(O-*t*-Bu)₄ and HO-*t*-Bu". James Caruso, Todd M. Alam and Mark J. Hampden-Smith, *Inorg. Chem.*, submitted Jan. 1995.
- "Preparation of Strontium Hexaferrite Fine Particles by Spray Pyrolysis." Yoshihide Senzaki, James Caruso, Mark J. Hampden-Smith, Toivo T. Kodas, and Lu-Min Wang, *J. Amer. Cer. Soc.*, **78**(11), 2973-76, 1995.
- "Comparison of a Congener Set of Alkali Metallated Titanium (IV) *Iso*-propoxide Complexes: X-ray Structures of [NaTi(OCHMe₂)₅]_∞ and [KTi(OCHMe₂)₅]_∞." Timothy J. Boyle, Donald C. Bradley, Mark J. Hampden-Smith, Anil Patel, and Joseph W. Ziller, *Inorg. Chem.*, **34**, 5893, 1995.
- "An Investigation of Alcohol-Alkoxide Exchange Between Sn(O-*t*-Bu)₄ and HO-*t*-Bu in Coordinating and Non-Coordinating Solvents". James Caruso, Todd M. Alam, Arnold L. Rheingold, Glenn Yap and Mark J. Hampden-Smith *Dalton Transactions*, 2659-2664, 1996.

- "Solution Routes to Metal Oxide Films Through Ester Elimination Reactions." James Caruso, Clive Chandler, Mark Hampden-Smith, submitted March, 1995, T. I. Docket #19997.
- "A Comparison of Solid-State and Aerosol Synthesis of Yttrium Aluminate Powders as a Function of Precursor Design." May Nyman, James Caruso, Toivo T. Kodas and Mark J. Hampden-Smith. *J. Amer. Chem. Soc.*, in press.
- "A Review of Group 2 (Ca, Sr, Ba) Metal-Organic Compounds as Precursors For Chemical Vapor Deposition (CVD)," in press, *Advances in Organometallic Chemistry*, Volume I, Editor, F. Gordon Stone, Mark J. Hampden-Smith, William A. Wojtczak, and Patrick Fleig.
- "Ester Elimination: A General Solvent Dependent Non-Hydrolytic Route to Metal and Mixed-Metal Oxides," J. Caruso, and M. J. Hampden-Smith, *J. Sol-Gel Sci.*, in press, 1996.

7. Interactions/Transitions:

a. Presentations at Meetings

- * a. "Synthesis of Homo and Heteronuclear μ -Oxo Bridged Metal Oxide Clusters: A General Alternative Non-Hydrolytic Sol-Gel Method for the Preparation of Oxide Ceramics," J. Caruso, C. Roger, M. J. Hampden-Smith, F. Schwertfeger, U. Schubert.
- b. "Aerosol Synthesis of Yttrium Aluminum Garnet [YAG] from a Novel Single-Source Precursor," May Nyman, James Caruso, Mark J. Hampden-Smith, Toivo T. Kodas. *Spring MRS Meeting*, San Francisco, 1994.
- * a. "Aerosol Synthesis Of Yttrium Aluminates from Inorganic and Metal-Organic Precursors," M. Nyman, James Caruso, M. J. Hampden-Smith, T. T. Kodas. annual meeting of the *American Society of Chemical Engineers*, San Francisco, 1994.
- * a. "Aerosol Synthesis Of Yttrium Aluminum Garnet [Yag] From A Novel Single-Source Precursor." May Nyman, James Caruso, Mark J. Hampden-Smith, Toivo T. Kodas, *Fourth International Aerosol Conference*, Los Angeles, 1994.
- * a. "Aerosol Routes to Fine Particles from Metal-Organic and Organometallic Precursors," Toivo T. Kodas, Mark Hampden-Smith. *American Chemical Society*, 208th ACS meeting, August 21-25, Washington D. C., 1994. (Invited Talk)
- * a. "Synthesis and Characterization of Perovskite Phase Mixed Oxides Formed by Molecular Routes," Clive D. Chandler, and Mark J. Hampden Smith, Paper #177, Fall *ACS Meeting*, Anaheim, CA, 1995.
- b. "Molecular Routes to Tin Sulfide Clusters Via Small Molecule Elimination Reaction", Klaus Kunze, James Caruso, Mark Hampden-Smith, Paper #474.
- * Ester Elimination Reactions In The Construction of Metal-Oxo Building Blocks to Inorganic Materials. James Caruso, Mark J. Hampden-Smith, 2nd International Materials Chemistry Conference, Canterbury, UK, July 1995. (Invited Talk)
- * The Role of Precursor Design in The Formation of Metal-OXO Clusters as Building Blocks for the Formation of Solid-State Materials. James Caruso, Mark J. Hampden-Smith, Fall ACS Meeting, PMSE division, Chicago, Aug., 1995. (Invited Talk)

b. Consultative and advisory functions

Interactions with Dick Stoltz at Texas Instruments who are interested in developing ester elimination reactions for the formation of perovskite phase materials. Texas Instruments have funded a program to investigate the formation of perovskite phase inorganic films via ester elimination.

c. Transitions

See b. above and section 8.

8. Patent disclosures

"Solution Routes to Metal Oxide Films Through Ester Elimination Reactions."
James Caruso, Clive Chandler, Mark Hampden-Smith, submitted March, 1995, T. I. Docket #19997. US patent application, filed by Texas Instruments who is interested in licensing this technology. This patent application was recently filed in other countries.

9. Honors/awards

Kipping Lectureship, University of Nottingham
Camille and Henry Dreyfus Teacher Scholar Award, 1993 - present
University of New Mexico Regents Lectureship, 1991 - 1994, 1995 - 1998.