

Precursors to Ultrathin Films of ZrO_2 Design on a Molecular Level

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Sol-gel derived thin films ($< 1 \mu\text{m}$) are the oldest and most widely used commercial application of sol-gel technology.¹ Films prepared by traditional sol-gel processing techniques have been utilized mainly for optical and electronic purposes.² Recently, submicron device miniaturization has created a demand for ultrathin ($< 100 \text{ \AA}$) oxide films.^{3,4} However, sol-gel chemistry involves the hydrolysis and condensation of molecular precursors to form polymeric intermediates having dimensions greater than 100 \AA ,⁵ making the traditional sol-gel approach unsuitable for the preparation of ultrathin films. The research presented in this seminar is concerned with the isolation, synthesis, and characterization of zirconium(IV) *n*-alkoxides and oxoalkoxides designed to serve as suitable molecular precursors for the preparation of zirconia films with thicknesses $< 100 \text{ \AA}$.

Tetra-*n*-propyl orthozirconate (**1**) was purified by vacuum distillation and isolated as a moisture sensitive, crystalline solid.⁶ According to a single crystal X-ray diffraction study, compound **1** has the same tetrameric structure observed previously for *n*-alkyl orthotitanates (Figure 1a).⁷⁻⁹ According to ^{13}C and ^1H NMR spectroscopy, the Zr_4O_{16} core structure was

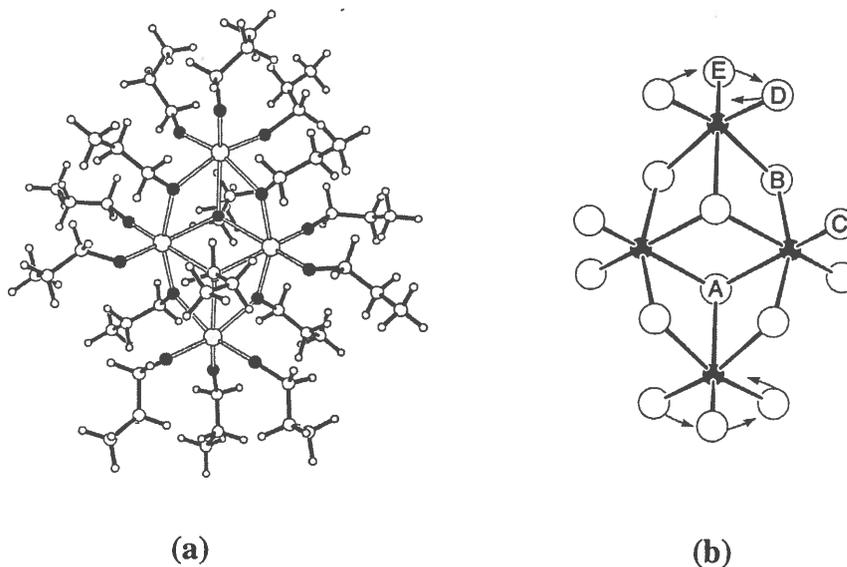


Figure 1

retained in hydrocarbon solution. A variable temperature ^{13}C NMR study of $\text{Zr}_4(\text{OPr}^n)_{16}$ in methylcyclohexane- d_{14} revealed an intramolecular dynamic process for **1** between -30 and $+5$ $^\circ\text{C}$ involving a twisting motion whereby two of the four octahedrally coordinated zirconium centers undergo degenerate exchange through a trigonal prismatic intermediate (Figure 1b).

Hydrolysis of tetra-*n*-propyl orthozirconate with 1.5 equiv of water in *n*-propanol under reflux yielded a new polyoxozirconate complex, *n*-propyl triskaidecázirconate, $[\text{Zr}_{13}\text{O}_8](\text{OH})_{12}(\text{OPr}^n)_{24}$ (**2**). A single crystal X-ray diffraction study of **2** revealed a $\text{Zr}_{13}\text{O}_{44}$ metal-oxygen framework (Figure 2) having a structure similar to that reported for the methyl-

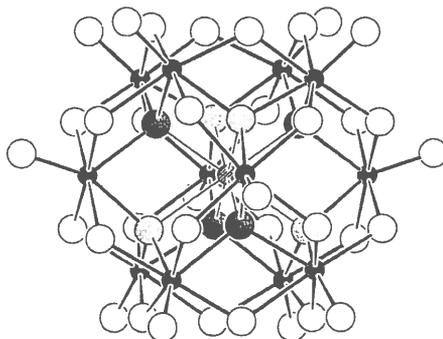


Figure 2

triskaidecázirconate, $[\text{Zr}_{13}\text{O}_8](\text{OMe})_{36}$.¹⁰ Here alkoxide oxygens are represented by large open circles and the two types of oxide oxygens are represented by large circles that are uniquely shaded. The central zirconium atom of **2** is tetrahedrally distorted from an octahedral cubic environment, and the $\text{Zr}_{13}\text{O}_{32}$ core structure of **2** (Figure 3a) is a fragment of tetragonal zirconia (Figure 3b). The twelve zirconium atoms in $[\text{Zr}_{13}\text{O}_8](\text{OH})_{12}(\text{OPr}^n)_{24}$ which surround the ZrO_8 oxide core are seven-coordinate and have a coordination environment analogous to that found in monoclinic zirconia. Hydrolysis of tetra-*n*-butyl orthozirconate under the same conditions yielded the *n*-butyl analog of *n*-propyl triskaidecázirconate.

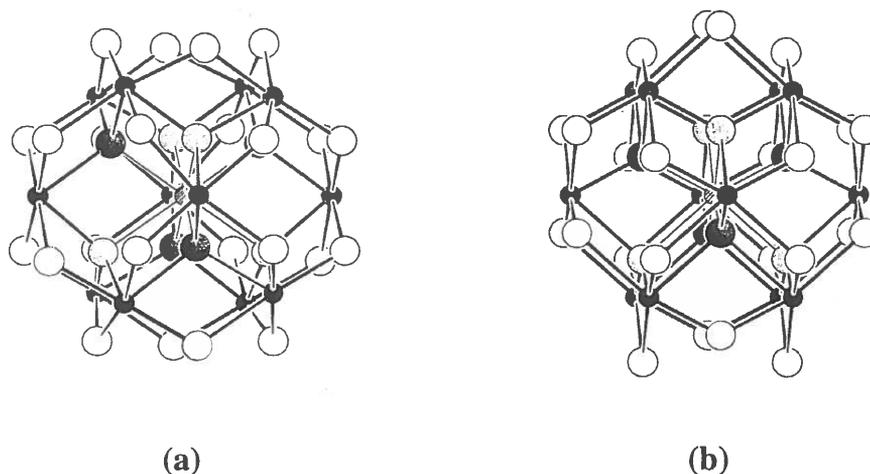


Figure 3

Ultrathin films of zirconia were obtained after the chemisorption and subsequent hydrolysis of $\text{Zr}_4(\text{OPr}^n)_{16}$ on the surface of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO). An increase in surface

zirconium was observed by XPS upon repeated cycles of adsorption and hydrolysis of the alkoxide. The zirconia films were shown to be chemically stable tunneling barriers between YBCO and a metal electrode and are currently being used to probe the superconducting mechanism of YBCO.¹¹

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