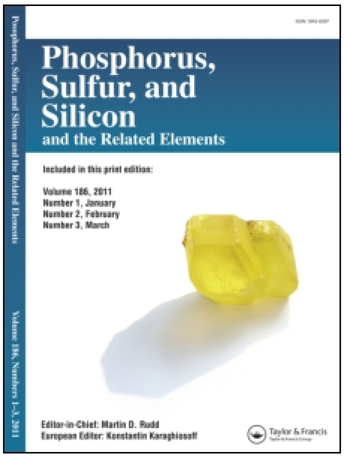

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Metal Organic Precursors for Yttria

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METAL ORGANIC PRECURSORS FOR YTTRIA

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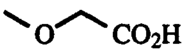
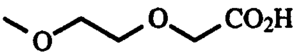
Abstract Several carboxylic acid derivatives of yttrium that have potential as metal organic deposition (MOD) precursors for yttria were prepared and characterized. These included a traditional MOD precursor bearing 2-ethylhexanoate ligands and a new class of precursors bearing poly-ether carboxylic acid ligands. Notably, the latter complexes are viscous liquids.

INTRODUCTION

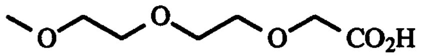
Metalorganic deposition (MOD)[1] is a non-vacuum liquid-based method of depositing thin films. Suitable metalorganic precursors are coated on a substrate using a variety of methods such as spin- or dip-coating or screen printing and they are then subsequently pyrolyzed to their constituent elements, oxides, or other compounds. Metal carboxylates are often used as MOD precursors for the preparation of ceramic oxides and processes for the generation of many oxide-based materials have already been developed: e.g. $BaTiO_3$ [2], $YBa_2Cu_3O_7$ [3] and ZrO_2 [4]. Furthermore, methodology has also been developed to achieve epitaxial growth of dense, polycrystalline, zirconia thin films [5]. Typically, the metal carboxylates used in the preparation of ceramic oxide materials are 2-ethylhexanoate or neodecanoate salts of the metals and they are dispersed as solutions in aromatic solvents. We report herein the synthesis and investigation of the thermal behavior of 2-ethylhexanoate (EtHx), methoxyacetate (MeOAc), 3,6-dioxaheptanoate (DOH), and 3,6,9-trioxadecanoic acid (TOD) complexes of yttrium.



MeOAc



DOH



TOD

RESULTS AND DISCUSSION

Yttrium tris(2-ethylhexanoate) was prepared by the reaction of yttrium carbonate and 2-ethylhexanoic acid in refluxing toluene. It was found that the reaction requires farly dilute conditions (ca. 0.2 M 2-ethylhexanoic acid in toluene) to prevent pyrolysis of the reaction intermediates on the side of the flask. As well, the reaction was greatly accelerated by the use of a Dean-Stark apparatus to remove the produced water. After a homogeneous solution is obtained, removal of the solvent affords the anhydrous yttrium carboxylate in quantitative yield.

The MeOAc, DOH, and TOD complexes of yttria were prepared by the aqueous reaction of yttrium carbonate with six-equivalents of the acids. They were isolated by evaporation of the water followed by extensive drying in a vacuum oven at 60 °C. All of the complexes were viscous liquids with the mobility increasing slightly with increasing chain length. They are extremely hydroscopic and even under the intensive drying conditions used they were isolated as the hydrates; $Y(MeOAc)_3(H_2O)_3$, $Y(DOH)_3(H_2O)_3$,and $Y(TOD)_3(H_2O)_3$. The complexes are soluble in water and all common polar organic solvents including methanol, ethanol, tetrahydrofuran, methylene chloride and acetonitrile. However, the solubility of the methoxyacetate complex tends to be much less than that of the polyether carboxylic acids. The ^1H and ^{13}C NMR spectra of the complexes obtained in the latter solvent indicated that all the carboxylic acid residues were in identical environments.

The thermal behavior of the various yttrium carboxylates was investigated by thermal gravimetric analysis coupled with differential thermal analysis. All complexes, with the exception of the 2-ethylhexanoate, begin to lose their waters of hydration at temperatures ranging from 110°C to 125°C. The decomposition of the ether-containing ligands occurs via two step-wise exothermic reactions. These occur at 259°C and 347°C for $Y(MeOAc)_3$, 277°C and 377°C for $Y(DOH)_3$, and 283°C and 385°C for $Y(TOD)_3$. Therefore, both exotherms show a progression to higher temperature with increasing chain-length. Unfortunately, the volatile species detected by simultaneous TGA-MS are simply water and carbon dioxide and further research is necessary to determine the thermochemistry of these compounds. The completion of the burn out of the organics for $Y(EtHx)_3$, $Y(MeOAc)_3(H_2O)_3$, $Y(DOH)_3(H_2O)_3$,and $Y(TOD)_3(H_2O)_3$ occurs at 510°C, 453 °C, 481°C, and 486°C, respectively. The corresponding ceramic yields are 21.7%, 27.5%, 20.8% , and 16.7%.

The above results suggest that the polyether carboxylic acids may serve as excellent ligands for MOD precursors. The fact that they are liquids means that they may be coated on substrates with little or no solvent. If solvents are required, more environmentally-friendly solvents than aromatic hydrocarbons may be used. As well, the pyrolysis of the ligands is completed at lower temperatures. Our initial attempts to place a thin-film of yttria on silicon by spin-coating and pyrolysis of $Y(DOH)_3(H_2O)_3$ in acetonitrile gave smooth, coherent coatings. Also, the bulk pyrolysis of this complex was performed at 600°C and was found to yield Y_2O_3 with a small crystallite size (23 nm).

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