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Studies on the Nature of a Lead Zirconate Titanate (PZT) Precursor Solution. Isolation and Structural Characterization of $[PbZr_2(O)(OOCCH_3)_2(OCH_2CH_3)_6]_2$

Linqing Ma and David A. Payne*

Department of Materials Science and Engineering
Materials Research Laboratory
and Beckman Institute
University of Illinois at Urbana—Champaign
Urbana, Illinois 61801

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Sol–gel processing of ceramic powders, fibers, and thin layers has attracted attention as an emerging technology for the possible control of stoichiometry, homogeneity, and reactivity of ceramic materials which can be processed at reduced temperatures.[1,2] Early success was reported for silicate systems, including optical glass and corrosion and scratch-resisting coatings, which were prepared from silicon alkoxides.[3] The underlying chemistry in the hydrolysis–condensation of orthosilicates was probed, and a fair understanding of the structural (including molecular and microstructural) evolution from sol to gel to glassy or crystalline ceramics was established.[4] More recent efforts have centered around the use of the sol–gel method to prepare nonsilicate multicomponent oxides, for example, ferroelectric, superconducting, and magnetic ceramics, in various shapes and forms.[5,6] However, our knowledge of the chemical processes is limited, as the properties of alkoxides of the highly electropositive elements are significantly different from those of silicon.[7]

Lead zirconate titanate (PZT, $PbZr_xTi_{1-x}O_3$, $x = 0$–1) crystalline solutions are industrially important electroceramics which find use in piezoelectric transducers, electromechanical actuators, and pyroelectric detectors.[8] At the present time, many research groups are attempting to integrate PZT-based ceramics in thin-layer form on substrate materials, including semiconductors, for nonvolatile computer memories, electrooptic connectors, and other microelectronic applications. Consequently, the use of various deposition methods, including sol–gel processing, is under investigation. However, detailed studies of the solution chemistry involved in sol–gel processing have lagged behind the development of technology. Previously reported characterization data for PZT precursor solutions were obtained by FT-IR and ^1H and ^{13}C NMR spectroscopies, from which only a limited amount of information was deduced on the exact structures of soluble metalloorganic species.[9–11] In reality, a large variety of metalloorganic starting materials have been used, together with additives and solvent systems, which were chosen primarily by empirical reasons. Concurrently, PZT thin layers with a wide range of electrical properties have been reported in the literature, making it impossible to isolate and control the effect of each individual processing parameter on the resulting microstructure–property rela-

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tions.[12] Therefore, it is obvious that a basic understanding of the chemistry, starting from the study of precursor solutions, to the development of desired crystalline microstructures, is ultimately necessary for the potential large scale manufacture of PZT thin layers with reproducible properties.

We have undertaken an investigation into the nature of a PZT precursor solution and the results are reported here. Anhydrous lead acetate ($Pb(OAc)_2$), zirconium tetraethoxide ($Zr(OEt)_4$), and titanium tetraethoxide ($Ti(OEt)_4$) were selected as starting materials due to their commercial availability and ease of preparation,[10] as well as our previous success in isolating a lead–titanium oxoacetatoethoxide complex $[PbTi_2(\mu_4\text{-}O)(OOCCH_3)(OCH_2CH_3)_7]_2$ from $Pb(OAc)_2$ and $Ti(OEt)_4$.[13] In addition, the same starting material combination with a proper additive has been used to prepare highly oriented PZT thin layers.[14] We observed that a homogeneous ethanol solution containing $Pb(OAc)_2$, $Zr(OEt)_4$, and $Ti(OEt)_4$ starting materials in a 2:1:1 ratio could be prepared by heating the cloudy suspension to reflux.[15] When the precursor solution was hydrolyzed with 2 equiv of water for each equivalent of lead atom ($R_w = 2$), an opaque gel formed quickly at room temperature, which could be transformed into the perovskite phase PZT ($x = 0.5$) after heat treatment between 600 and 700 °C. By cooling the same precursor solution, a white polycrystalline solid was isolated and vacuum dried. The dried powder was no longer soluble in any organic solvents, including the parent ethanol, even under boiling conditions. Therefore, characterization was limited to elemental analysis and IR spectroscopy.[16] Results of the former experiment indicated this compound contained lead as the only metal element, and the IR spectrum of this lead-only compound was identical to that of $Pb(OAc)_2$. This possibly suggests that not all the $Pb(OAc)_2$ reacted with Zr and Ti ethoxides to form heterometallic complexes with the 2:1:1 composition (i.e., PZT 50/50).

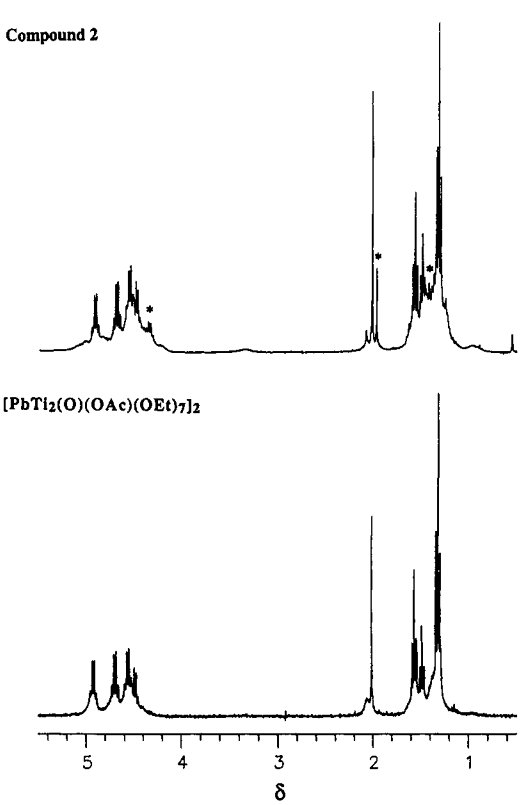

Figure 1. Comparison of the ^1H NMR (benzene-d_6, 20 °C) spectra of compound **2** isolated from the PZT precursor solution and authentic $[PbTi_2(\mu_4\text{-}O)(OOCCH_3)(OCH_2CH_3)_7]_2$. Resonances labeled with * are due to contamination from compound **1**.

The dissolution behavior of 2 mol of $Pb(OAc)_2$ in an ethanol solution of 1 mol of $Zr(OEt)_4$ and 1 mol of $Ti(OEt)_4$ (i.e., where heating was necessary for the formation of a clear solution), and the isolation of unreacted $Pb(OAc)_2$ from this solution, prompted us to examine the reaction of $Pb(OAc)_2$, $Zr(OEt)_4$, and $Ti(OEt)_4$ in a 1:1:1 ratio. Thus, when a solution of zirconium and titanium ethoxides prepared by heating in refluxing ethanol was combined with an ethanol suspension of $Pb(OAc)_2$ in the prescribed stoichiometry, a clear solution formed within minutes at room temperature after the completion of solution transfer, indicating the formation of heterometallic species which requires a complete consumption of

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(12) See, for example: (a) Fukushita, J.; Kodaira, K.; Matsushita, T. *J. Mater. Sci.* **1984**, *19*, 595. (b) Yi, G.; Wu, Z.; Sayer, M. *J. Appl. Phys.* **1988**, *64*, 2717. (c) Peng, C. H.; Park, S. W.; Desu, S. B. In *Ferroelectric Thin Films*; Myers, E. R., Kingon, A. I., Eds.; Materials Research Society: Pittsburgh, PA, 1990. (d) Gupta, A.; Dey, S. K. In *Ferroelectric Thin Films*; Myers, E. R., Kingon, A. I., Eds.; Materials Research Society: Pittsburgh, PA, 1990. (e) Tohge, N.; Takahashi, S.; Minami, T. *J. Am. Ceram. Soc.* **1991**, *74*, 67. (f) Carim, A.; Tuttle, B. A.; Doughty, D. H.; Martinez, S. L. *J. Am. Ceram. Soc.* **1991**, *74*, 1455. (g) Hsueh, C.-C.; Mecartney, M. L. *J. Mater. Res.* **1991**, *6*, 2208. (h) Klee, M.; Eusemann, R.; Waser, R.; Brand, W. *J. Appl. Phys.* **1992**, *72*, 1566. (i) Selvaraj, U.; Brooks, K.; Prasadarao, A. V.; Komarneni, S.; Roy, R.; Cross, L. E. *J. Am. Ceram. Soc.* **1993**, *76*, 1441.

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(15) In a typical procedure, $Zr(OEt)_4$ (0.835 g, 3.08 mmol) and $Ti(OEt)_4$ (0.701 g, 3.08 mmol) were first mixed with dry EtOH (60.0 mL). The cloudy solution was heated to reflux for 2 h to give a clear solution. The cooled solution was added to a flask containing solid $Pb(OAc)_2$ (2.000 g, 6.16 mmol), which resulted in a cloudy mixed suspension upon stirring at ambient temperature. The solution was again brought to reflux and maintained for 2 h after a clear solution had formed. The solvent was removed in vacuo to give a white powder, which was redissolved in EtOH (20.0 mL) with oil bath warming.

(16) The ethanol solution prepared in footnote 15 was cooled to 0 °C overnight, resulting in the formation of a white crystalline solid. The supernatant was removed and the solid was washed with 3 × 5 mL of dry EtOH and dried under vacuum. Yield: 0.401 g. Partial characterization of the solid: IR (KBr) 1561 (s, sh), 1522 (vs), 1411 (vs), 1333 (m), 1043 (vw), 1017 (w), 933 (vw), 806 (vw), 661 (m), 617 (w), 461 (vw), 417 (w) cm^{-1}. Anal. Calcd for $C_4H_6O_4Pb$ ($Pb(OAc)_2$): C, 14.77; H, 1.86; Pb, 63.70. Found: C, 13.31; H, 1.82; Pb, 62.21.

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(20) An ethanol solution containing $Zr(OEt)_4$ (0.839 g, 3.09 mmol) and $Ti(OEt)_4$ (0.708 g, 3.10 mmol) was prepared and combined with $Pb(OAc)_2$ (1.000 g, 3.07 mmol) with stirring. A clear solution formed at room temperature within 10 min. The solution was heated to reflux for 2 h and cooled to room temperature before all solvent was removed in vacuo. The white powder was extracted with dry heptane, giving a clear solution with a small amount of white residue. The solution was filtered and cooled to −20 °C. A white crystalline solid (**1**) formed in 3 days, which was separated from the mother liquor, washed with 2 mL of heptane and dried (0.168 g). Anal. Calcd for $C_{14}H_{36}PbZr_2O_{11}$: C, 24.20; H, 4.57, Pb, 26.09; Zr, 22.98. Found: C, 23.47; H, 4.48; Pb, 25.35; Zr, 23.12. IR (KBr): 2964 (s), 2916 (m), 2856 (m), 2701 (w), 1579 (s), 1555 (s), 1477 (s), 1441 (s), 1411 (s, sh), 1375 (m), 1148 (vs), 1100 (s), 1058 (vs), 897 (m), 801 (vw), 689 (w), 645 (w), 615 (m), 550 (s), 514 (s), 478 (s), 448 (s) cm^{-1}. ^{207}Pb NMR (benzene-d_6, 20 °C, ppm vs $PbMe_4$) −257 (s), −271 (s), −529 (s). The mother liquor was concentrated and further cooled to −20 °C. Another crystalline solid (**2**) was isolated after 1 week (0.082 g). ^1H NMR spectrum (benzene-d_6, 20 °C) of solid **2** was identical to that reported for $[PbTi_2(\mu_4\text{-}O)(OAc)(OEt)_7]_2$.[13]

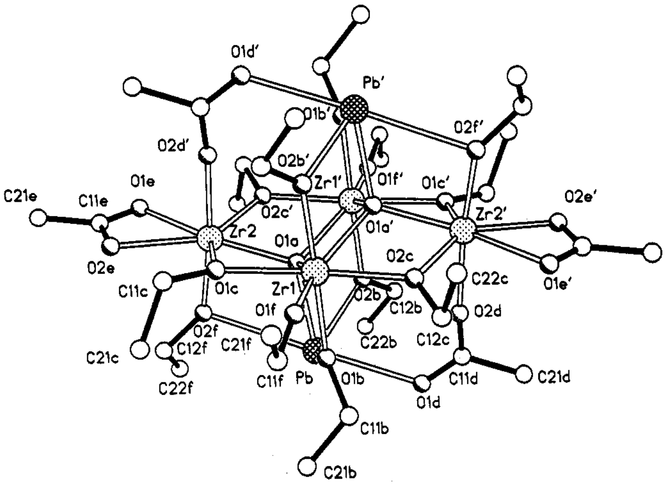

Figure 2. Perspective drawing of $[PbZr_2(\mu_4\text{-}O)(OOCCH_3)_2(OCH_2CH_3)_6]_2$. Selected average M-O bond lengths (Å): Pb-μ_4-O, 2.32; Pb-μ-O(Ac), 2.60; Pb-μ-O(Et), 2.46; Zr-μ_3-O, 2.17; Zr-μ-O(Ac) (chelating), 2.29; Zr-μ-O(Ac), 2.11; Zr-μ-O(Et), 2.13; Zr-μ-O(Et), 1.99.

$Pb(OAc)_2$. The observation was similar to previous reports for the dissolution of alcohol-insoluble metal acetates, such as $Pb(OAc)_2$,[13,17] $Cd(OAc)_2$,[18] and $Gd(OAc)_3$,[19] and the formation of heterometallic complexes. From the present reaction mixture, two white crystalline solids were separated and characterized.[20] ^1H NMR spectroscopy confirmed one of these species (2) to be the known compound $[PbTi_2(\mu_4\text{-}O)(OOCCH_3)(OCH_2CH_3)_7]_2$ (see Figure 1).[13] The other compound (1) is a new species, which contains lead and zirconium in a 1:2 ratio as determined by elemental analysis.

Formulation and structural characterization of compound 1 was achieved by a single-crystal diffraction study.[21] It is revealed that the discrete molecule has the formula of $[PbZr_2(\mu_4\text{-}O)(OOCCH_3)_2(OCH_2CH_3)_6]_2$ and adopts a $M_2M'_4$ dimeric structure.[22] A perspective drawing of the molecule without the hydrogen atoms is shown in Figure 2. Each of the two halves of the molecule is connected to the other by one bridging acetate ligand (O1d/O2d–C11d–C21d), one oxo ligand (O1a), and two bridging ethoxy groups (O2b–C12b–C22b and O2c–C12c–C22c). Alternatively, the structure can be viewed as two upside down "$PbZr_3(\mu_3\text{-}O)$" tetrahedra fused at a hypothetical Zr1–Zr1' edge. It is noteworthy that $PbZr_3(\mu_4\text{-}O)(OAc)_2(OPr^i)_{10}$ has been reported,[17] and compound 1 is related to it by the elimination of two $Zr(OEt)_4$ molecules upon dimerization. In fact, the lead cations in both compounds have a pentacoordination geometry. In addition, the average value for the various types of metal–oxygen bonds lengths are very similar (see caption for Figure 2). However, a major difference does exist between these two lead–zirconium complexes in that each zirconium atom in $PbZr_3(\mu_4\text{-}O)(OAc)_2(OPr^i)_{10}$ has six surrounding oxygen anions while in compound 1 the zirconium cations are heptacoordinated. The difference in coordination number for zirconium between the two compounds may arise from steric reasons, i.e., the metal cations require maximum space filling in their ligand spheres and OPr^i and OEt groups have different abilities to fulfill this requirement. It is also noteworthy that if the heptacoordination around Zr cations is preserved after $[PbZr_2(\mu_4\text{-}O)(OAc)_2(OEt)_6]_2$ undergoes hydrolysis and condensation, it may present an obstacle to perovskite phase development from the gel because a reduction in oxygen coordination number from seven to six is required.

The presence of an oxo ligand in $[PbZr_2(\mu_4\text{-}O)(OAc)_2(OEt)_6]_2$ is in good agreement with the observation that reactions of $Pb(OAc)_2$ and $Ti(OR)_4$ or $Zr(OR)_4$ lead to spontaneous formation of oxo ligands by elimination of ester or ether molecules from acetato and alkoxy ligands.[13,17] The loss of a molecule of diethyl ether from two ethoxy groups may explain the origin of the oxo ligand in compound 1 since all acetate groups originated from $Pb(OAc)_2$ are retained in the bimetallic species.

NMR studies indicat that compound 1 is not stable in solution and more than one species exists in solution, even when a nonpolar solvent is used, such as toluene. At ambient and low (−90 °C) temperatures both the ^1H and ^{13}C NMR spectra of 1 are too complex to allow for an individual listing of each resonance in footnote 20; however, the observation of three singlets by ^{207}Pb NMR spectroscopy indicates three species have formed as 1 dissociates. A similar behavior of instability in solution for a heterometallic alkoxide was reported for $Pb_6Nb_4(O)_4(OEt)_{24}$.[23]

The compositional heterogeneity indicated for the ethoxide based PZT precursor solution may be characteristic of other PZT formulations and account for the relatively high crystallization temperatures (600–700 °C) for this chemically derived compound compared with that of $LiNbO_3$ (perovskite phase crystallizes at 450 °C).[24] In the latter case, homogeneity in the molecular precursor stage is achieved through the formation of a bimetallic alkoxide with the correct stoichiometry. The implication of these results is under investigation.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles for non-hydrogen atoms (10 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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(21) Single crystals of compound 1 suitable for X-ray studies were grown slowly from a dilute heptane solution at −20 °C. Crystal structure was determined by Crystalytics Co., Lincoln, NE. The sample crystal (0.38 × 0.42 × 0.60 mm) was sealed inside a thin-walled glass capillary. A total of 4880 independent absorption-corrected (μ_a(Mo Kα) = 7.10 mm^{-1}) reflections having 2θ (Mo Kα) < 50.7° were collected on a computer-controlled Nicolet autodiffractometer at 20 ± 1 °C using full (0.90° wide) ω scans and graphite-monochromated Mo Kα radiation. The structure was solved using "Direct Methods" techniques with the Siemens SHELXTL-PC software package as modified at Crystalytics Company. The resulting structural parameters have been refined to convergence $\{R_1$(unweighted, based on F) = 0.052 for 2823 independent absorption-corrected reflections having 2θ (Mo Kα) < 50.7° and $I > 3\sigma(I)\}$ using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were not included in the structural model. Crystallographic data: triclinic, space group $P\bar{1}$ (No. 2) with a = 11.572 (3) Å, b = 11.920 (4) Å, c = 12.455 (4) Å, α = 61.84 (2)°, β = 89.30 (2)°, γ = 65.03 (2)°, V = 1335.0 (7) Å^3, Z = 1.

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