Formation of Crystalline, Integral, and Nonintegral Stoichiometry Perovskite-Phase Complex Metal Oxide Powders from Metal–Organic Precursors

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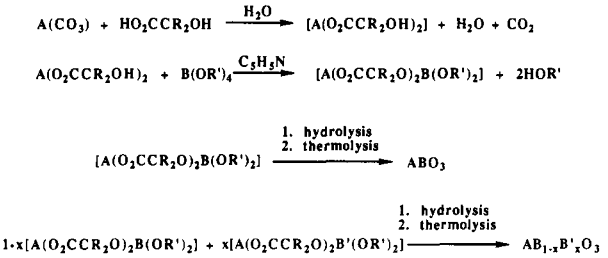
Perovskite-phase metal oxide ceramics exhibit a variety of interesting physical properties that are potentially useful for a number of applications.[1-3] Since these physical properties rely on the crystallinity and the crystallization behavior of these materials, extensive efforts have been devoted to the study of these aspects. Furthermore, the formation of crystalline, phase-pure materials at low temperatures is desired for thin-film applications.

A variety of methods of preparation of these materials have been explored. The industrial routes to $BaTiO_3$ powder involve the thermal reaction (800–1100 °C) between $BaCO_3$ and TiO_2 or the thermal decomposition of $BaTiO(C_2O_4)_2{\cdot}4H_2O$. Hydrothermal synthesis of $BaTiO_3$ powder has been achieved at much lower temperatures (150–200 °C) by reaction between barium and titanium hydroxides[4] in strongly alkaline (pH > 12) solutions in an autoclave at >5 MPa or from barium titanium acetate gels.[5] However, the materials produced by this method exhibit some anomalous behavior thought to be derived from the incorporation of water and the presence of hydroxyl groups in the crystal lattice.[6] Liquid-phase chemical approaches to perovskite-phase materials through metal–organic precursors have been extensively studied[2,3,7-11] and generally involve the reaction between metal alkoxides and metal carboxylates[7-9,11] followed by hydrolysis and thermally induced condensation/crystallization in the temperature range 400–700 °C. Some perovskite-phase materials have been crystallized at lower temperatures including $BaTiO_3$ (50 °C, 12 h[12] and 100 °C, unspecified time[13]) and $PbTiO_3$ (375 °C, 10 h).[14] A more recent report[15] has shown that crystalline $PbTiO_3$ can be formed by heating the product of the reaction between lead acetate and titanium ethoxide in an O_2 atmosphere for 1 h at 250 °C. On the basis of the TGA data presented, it seems likely that these conditions induce an exothermic reaction perhaps resulting in locally higher temperatures. Liquid-phase routes are especially useful because either films or powders may be produced by this method.[7]

Scheme I



$$A(CO_3) + HO_2CCR_2OH \xrightarrow{H_2O} [A(O_2CCR_2OH)_2] + H_2O + CO_2$$

$$A(O_2CCR_2OH)_2 + B(OR')_4 \xrightarrow{C_5H_5N} [A(O_2CCR_2O)_2B(OR')_2] + 2HOR'$$

$$[A(O_2CCR_2O)_2B(OR')_2] \xrightarrow[\text{2. thermolysis}]{\text{1. hydrolysis}} ABO_3$$

$$1{\cdot}x[A(O_2CCR_2O)_2B(OR')_2] + x[A(O_2CCR_2O)_2B'(OR')_2] \xrightarrow[\text{2. thermolysis}]{\text{1. hydrolysis}} AB_{1{\cdot}x}B'_xO_3$$

Here, we report a general, liquid-phase route which ultimately leads to the formation of crystalline, perovskite-phase mixed metal oxide powders at low temperatures. This method involves the reaction between metal–organic compounds that are specifically designed to react with each other to form controlled stoichiometry intermediates which are then susceptible to subsequent hydrolysis and condensation. Furthermore, it is demonstrated that this strategy also accommodates retention of molecular level homogeneity in the synthesis of *nonintegral* stoichiometry crystalline metal oxide materials at low temperatures via reactions between controlled stoichiometry precursors.

The preparation and characterization of lead(II) glycolate, $Pb(O_2CCR_2OH)_2]$, was recently reported.[16] This species is an example of a larger class of divalent metal α-hydroxycarboxylates of general empirical formula $A(O_2CCR_2OH)_2$ where A = Pb, Ca, Sr, Ba and R = H, Me.[17] These species are designed to react with metal alkoxide compounds such as $B(OR')_4$, where B = Ti, Zr, Sn, with the elimination of 2 equiv of alcohol to form species with a fixed A:B stoichiometry of 1:1 according to eq 1. When

$$A(O_2C(CR_2)OH)_2 + B(OR')_4 \rightarrow A(O_2CCR_2O)_2B(OR')_2 + 2HOR' \quad (1)$$

the reaction of eq 1 (R = H) was carried out in either the parent alcohol (R′OH) or with pyridine as solvent, a white precipitate was formed, but further characterization was hampered by the extremely low solubility of this solid.

When the reactions of eq 1 where R = Me are carried out, the solubility of the reaction products in pyridine increased markedly to give homogeneous clear solutions.[18,19] ^1H NMR data showed that the liberated alcohol

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[18] A typical example is described here: 0.740 g (1.79 mmol) of $Pb(O_2CCMe_2OH)_2$ was dissolved in 30 mL of dry pyridine, and 0.510 g (1.79 mmol) of $Ti(O\text{-}i\text{-}Pr)_4$ was added with rapid stirring at room temperature to give a clear solution with a small amount of precipitate. An excess of water (0.8 g) was added, and after an initial precipitation, the solids redissolved and the solution became transparent again with all the solid dissolved. The volatile components were removed in vacuo and a white solid was obtained. TGA data are consistent with the formation of $A(O_2CCMe_2O)_2B(OH)_2$, at this stage, e.g., $Ba(O_2CCMe_2O)_2Ti(OH)_2$, → $BaTiO_3$ weight loss calcd = 54.9%, obsd = 52.5%. A portion of this solid was transferred to a Pyrex crucible and heated at 350 °C for 0.5 h in an oxygen atmosphere. The X-ray diffraction patterned obtained indicated the presence of perovskite-phase $BaTiO_3$.

was coordinated to the complex and pyridine was present, consistent with the empirical formula $A(O_2CCR_2O)_2B(OR')_2 \cdot 2HOR' \cdot xC_5H_5N$.[19] However, elemental analysis and TGA data were more consistent with the empirical formula $A(O_2CCR_2O)_2B(OR')_2 \cdot x(C_5H_5N)$.[19] Furthermore, addition of an excess of water to these rapidly stirred solutions often resulted in initial precipitation followed by rapid redissolution to form transparent homogeneous solutions. Evaporation of the volatile components in vacuo from these solutions gave either white or pale yellow solids.[20] Elemental analyses were consistent with the empirical formula $A(O_2CCR_2O)_2B(OH)_2 \cdot x(H_2O) \cdot x(C_5H_5N)$.[20] ^1H NMR and ^{13}C NMR data confirmed that the alkoxide and alcohol ligands had been removed but the glycolate ligands were still present. Thermogravimetric analysis of these solids carried out in air and in oxygen revealed that the weight loss is always complete at lower temperatures in an oxygen atmosphere. In O_2, weight loss was complete between 300 and 400 °C and was consistent with formation of the corresponding metal oxide, ABO_3. In air, initial weight loss occurred at similar temperatures, but additional weight loss was often observed at higher temperatures, typically between 600 and 700 °C. This higher temperature weight loss corresponded to the loss of CO_2 and is presumed to be derived from the formation of metal carbonates probably derived from atmospheric CO_2; see Figure 1. If the unhydrolyzed material, $A(O_2CCR_2O)B(OR')_2$, is heated directly or hydrolysis was carried out in the solid state in air, TGA in O_2 showed retention of the high-temperature weight loss step. Therefore, it appears that homogeneous hydrolysis in pyridine, removal of the volatile components in vacuo, and subsequent thermolysis in O_2 are the optimum reaction conditions based on TGA data. The isolated, hydrolyzed intermediate solids are quite soluble in water and water/alcohol mixtures.

Thermolysis of bulk samples of the crude mixed metal hydrolysis products at 350 °C revealed that, in all cases, crystalline phases had been formed. For example, thermolysis of the hydrolysis product from the reaction of $Pb(O_2CCMe_2OH)_2$ and $Ti(O\text{-}i\text{-}Pr)_4$ formed crystalline perovskite phase $PbTiO_3$ with a small amount of crystalline PbO as impurity, as shown in Figure 2. The sharp diffraction peaks indicate the presence of large (>1000 Å) crystallites. All other representative species examined ($BaSnO_3$, $CaTiO_3$, and $BaTiO_3$) exhibited large crystallite sizes except $PbZrO_3$ which on heating even to 400 °C for 0.5 h exhibited broad diffraction maxima corresponding to a crystallite size of ~30 nm.

To examine the potential of this method for the formation of nonintegral stoichiometric materials via reactions between mixtures of stoichiometric precursors, one representative example of the system $AB_{1-x}B'_xO_3$ was investigated. Pyridine solutions of the hydrolysis products derived from the reactions between $Pb(O_2CCMe_2OH)_2$ and $Ti(O\text{-}i\text{-}Pr)_4$, and between $Pb(O_2CCMe_2OH)_2$ and $Zr(O\text{-}i\text{-}Pr)_4$ were mixed in the mole ratio 0.48:0.52, respectively.[19-21] This ratio was chosen because it should be possible to distinguish the formation of a mixture of phases (i.e., $PbTiO_3$ *and* $PbZrO_3$) from the formation of the known crystalline single-phase product $PbZr_{0.52}Ti_{0.48}O_3$ by X-ray powder diffraction. After mixing, the homogeneous transparent solution was stirred for 5 min., the volatile components were removed in vacuo and the pale orange solid was heated to 350 °C in O_2. The X-ray powder diffraction data for the yellow solid obtained under these conditions is shown in Figure 3. This diffraction pattern reveals only the presence of crystalline perovskite phase $PbZr_{0.52}Ti_{0.48}O_3$. A similar strategy using a mixture of Sr and Ba precursors gave $Ba_{0.6}Sr_{0.4}TiO_3$ as the only crystalline phase.

In summary, while it is clear that there are a number of questions to be addressed, particularly concerning the solution chemistry and whether other amorphous materials are present after heating to these temperatures, the

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[19] Representative characterization data: $\mathit{Ba(O_2CC(CH_3)_2O)_2Ti(OPr^i)_2}(HOPr^i)_2\mathit{(C_5H_5N)_x}$: ^1H NMR (pyridine-d_5, 300 K, 250 MHz) 5.73 ppm (1 H, d, ^3J = 4.2 Hz, $\mathit{H}OCH(CH_3)_2$), 4.64 ppm (1 H, septet, ^3J = 6.0 Hz $OC\mathit{H}(CH_3)_2$), 4.16 ppm (1 H, d × septet, ^3J = 6.0 Hz, $HOC\mathit{H}(CH_3)_2$), 1.27 ppm (18 H, overlapping mult, $HOCH(C\mathit{H}_3)_2$, $O_2CC(C\mathit{H}_3)_2O$). IR (KBr pellet) 3224 (m), 2973 (s), 2922 (s), 2862 (s), 1636 (vs), 1463 (s) 1442 (s), 1378 (s), 1261 (m), 1205 (s), 1105 (s), 1123 (s), 1069 cm^{-1} (s). Elemental anal. Calcd for $Ba(O_2CC(CH_3)_2O)_2Ti(OPr^i)_2(C_5H_5N)_x$, $C_{19}H_{31}O_8NBaTi$: 38.9% C, 5.3% H, 2.4% N. Found: 37.7% C, 5.0% H, 2.4% N. $Pb(O_2CC(CH_3)_2O)_2Ti(OPr^i)_2(HOPr^i)_2(C_5H_5N)_x$: ^1H NMR (pyridine-d_5, 300 K, 250 MHz) 5.72 ppm (1 H, d, ^3J = 3.3 Hz, $\mathit{H}OCH(CH_3)_2$), 5.4 ppm (1 H, mult, $OC\mathit{H}(CH_3)_2$) 5.01 (1 H, septet, $OC\mathit{H}(CH_3)_2$) 4.64 ppm (2 H, septet, ^3J = 6.0 Hz $OC\mathit{H}(CH_3)_2$), 4.16 ppm (1 H, d × septet, ^3J = 4.2 Hz, ^3J = 6.0 Hz, $HOC\mathit{H}(CH_3)_2$), 1.27 ppm (overlapping mult, $HOCH(C\mathit{H}_3)_2$, $O_2CC(CH_3)_2O$). IR (KBr pellet) 3423 (w), 2970 (vs), 2928 (s), 2864 (s), 1605 (vs), 1464 (s), 1448 (s), 1377 (vs), 1358 (sh), 1326 (s), 1202 (vs), 1163 (vs), 1126 (vs), 1068 (m), 990 cm^{-1} (vs). Elemental Anal. Calcd for $Pb(O_2CC(CH_3)_2O)_2Ti(OPr^i)_2(C_5H_5N)_x$, $C_{19}H_{31}O_8NPbTi$: 38.8% C, 4.8% H, 2.1% N. Found: 34.5% C, 5.1% H, 2.4% N. $\mathit{Ca(O_2CC(CH_3)_2O)_2Ti(OPr^i)_2(HOPr^i)_2(C_5H_5N)_x}$: ^1H NMR (pyridine-d_5, 300 K, 250 MHz) 5.74 (1 H, d, ^3J = 2.6 Hz, $\mathit{H}OCH(CH_3)_2$), 5.15 ppm (1 H, mult, $OC\mathit{H}(CH_3)_2$), 4.90 ppm (1 H, mult, $OC\mathit{H}(CH_3)_2$), 4.65 ppm (1 H, septet, ^3J = 6.0 H $OC\mathit{H}(CH_3)_2$), 4.16 ppm (1 H, d × septet, ^3J = 4.2 Hz, ^3J = 6.0 Hz, $HOC\mathit{H}(CH_3)_2$), 1.27 ppm (18 H, overlapping mult, $HOCH(C\mathit{H}_3)_2$, $O_2CC(CH_3)_2O$). IR (KBr pellet) 3213 (w), 2973 (vs), 2929 (s), 2866 (s), 1616 (vs), 1466 (s), 1444 (s), 1378 (vs), 1362 (vs), 1331 (s), 1205 (vs), 1164 (vs), 1124 (vs), 988 (vs). Elemental anal. Calcd for $Ca(O_2CC(CH_3)_2O)_2Ti(OPr^i)_2(C_5H_5N)_x$, $C_{19}H_{31}O_8NCaTi$: 46.6% C, 6.4% H, 2.9% N. Found: 45.7% C, 6.0% H, 2.9% N. $\mathit{Pb(O_2CC(CH_3)_2O)_2Zr_{0.52}Ti_{0.48}(OPr^i)_2(HOPr^i)_2(C_5H_5N)_x}$: ^1H NMR (pyridine-d_5, 300 K, 250 MHz) 5.78 ppm (1 H, d, ^3J = 3.3 Hz, $\mathit{H}OCH(CH_3)_2$), 4.65 ppm (1 H, septet, ^3J = 6.0 Hz $OC\mathit{H}(CH_3)_2$), 4.16 ppm (1 H, d × septet, ^3J = 4.2 Hz, ^3J = 4.2 Hz, ^3J = 6.0 Hz, $HOC\mathit{H}(CH_3)_2$), 1.27 ppm (18 H, overlapping mult, $HOCH(C\mathit{H}_3)_2$, $O_2CC(C\mathit{H}_3)_2O$). IR (KBr pellet) 2969 (vs), 2928 (s), 2863 (m), 1597 (vs), 1464 (s), 1440 (s), 1375 (vs), 1329 (s), 1201 (vs), 1163 (vs), 1126 (s), 1068 (m), 979 cm^{-1} (vs).

[20] Representative characterization data: $\mathit{Ba(O_2CC(CH_3)_2O)_2Ti(OH)_2(C_5H_5N)_x}$: ^1H NMR (D_2O, 300 K, 250 MHz) 1.21, 1.20 ppm (s, $O_2CC(C\mathit{H}_3)_2OH$). $^{13}C\{^1H\}$ NMR (D_2O with benzene-d_6 internal reference, 300 K, 62.9 MHz) 191.0, 184.7 (s, $O_2\mathit{C}C(CH_3)_2OH$), 88.1, 74.4 (s, $O_2C\mathit{C}(CH_3)_2OH$), 27.4, 26.94 ppm (s, $O_2CC(\mathit{C}H_3)_2OH$). IR (KBr pellet) 3386 (s), 2976 (s), 1640 (vs), 1466 (m), 1379 (vs), cm^{-1} 1342 (s). Elemental anal. Calcd for $Ba(O_2CC(CH_3)_2O)_2Ti(OH)_2(C_5H_5N)_{0.5}(H_2O)_4$, $C_{10,5}H_{22,5}O_9N_{0,5}BaTi$: 25.2% C, 4.4% H, 1.3% N. Found: 25.2% C, 2.8% N, 1.0% N. $\mathit{Pb(O_2CC(CH_3)_2O)_2Ti(OH)_2(C_5H_5N)_x}$: ^1H NMR (D_2O, 300 K, 250 MHz) 1.23, 1.21 ppm (s, $O_2CC(C\mathit{H}_3)_2OH$). $^{13}C\{^1H\}$ NMR (D_2O with benzene-d_6 internal reference, 300 K, 62.9 MHz) 188.4, 182.9 (s, $O_2\mathit{C}C(CH_3)_2OH$), 85.6, 72.6 (s, $O_2C\mathit{C}(CH_3)_2OH$), 25.1 ppm (mult, $O_2CC(\mathit{C}H_3)_2OH$). IR (KBr pellet) 3421 (m), 2974 (s), 2930 (m), 1636 (vs), 1553 (s), 1460 (m), 1441 (m), 1376 (s), 1353 (s), 1332 (s), 1199 (vs), 1161 (s), 982 cm^{-1} (s). $\mathit{Ca(O_2CC(CH_3)_2O)_2Ti(OH)_2(C_5H_5N)_x}$: ^1H NMR (D_2O, 300 K, 250 MHz) 1.21 ppm, 1.20 ppm (s, $O_2CC(C\mathit{H}_3)_2OH$). $^{13}C\{^1H\}$ NMR (D_2O with benzene-d_6 internal reference, 300 K, 62.9 MHz) 188.4, 182.2 (s, $O_2\mathit{C}C(CH_3)_2OH$), 85.6, 72.4 (s, $O_2C\mathit{C}(CH_3)_2OH$), 24.4 ppm (mult, $O_2CC(\mathit{C}H_3)_2OH$). IR (KBr pellet) 3411 (s), 2979 (s), 2932 (s), 1639 (vs), 1465 (m), 1442 (m), 1380 (vs), 1357 (s), 1340 (s), 1203 (vs), 1180 (s), 1165 (s), 986 cm^{-1} (s). Elemental anal. Calcd for $Ca(O_2CC(CH_3)_2O)_2Ti(OH)_2(C_5H_5N)_{0,5}(H_2O)_3$, $C_{10.5}H_{20.5}O_9N_{0.5}CaTi$: 32.7% C, 5.3% H, 1.8% N. Found: 33.4% C, 5.3% H, 1.8% N. $\mathit{Pb(O_2CC(CH_3)_2O)_2Zr_{0.52}Ti_{0.48}(OH)_2(C_5H_5N)_x}$: ^1H NMR (D_2O, 300 K, 250 MHz) 1.20, 1.17 ppm (s, $O_2CC(C\mathit{H}_3)_2OH$). IR (KBr pellet) 3245 (s), 2976 (vs), 2926 (vs), 1622 (vs), 1465 (s), 1380 (vs), 1331 (vs), 1193 (vs), 1160 (vs), 1068 (w), 1032 (w), 982 cm^{-1} (vs).

[21] A 1:1 Pb:Zr solution was prepared as follows: 0.510 g (1.23 mmol) of $Pb(O_2CCMe_2OH)_2$ was dissolved in 30 mL of dry pyridine, and 0.400 g (1.23 mmol) of $Zr(O\text{-}i\text{-}Pr)_4$ was added with rapid stirring at room temperature to give a clear solution with a small amount of precipitate. An excess of water (0.8 g) was added, and after an initial precipitation, the solid redissolved and the solution became transparent again. The volatile components were removed in vacuo and a white solid was obtained. 18 mL (0.87 mmol) of this solution was then added to a Schlenk flask containing 14 mL (0.8 mmol) of the solution prepared in ref 15. This ratio corresponds to a Zr:Ti mole ratio of 0.52:0.48. The solutions were stirred for 5 min (and remained transparent with no precipitate). The volatile components were removed in vacuo and a pale orange solid was obtained. A portion of this solid was transferred to a pyrex crucible and heated at 350 °C for 0.5 h in an oxygen atmosphere. The X-ray diffraction patterned showed the presence of perovskite phase $PbZr_{0.52}Ti_{0.48}O_3$ and is shown in Figure 3.

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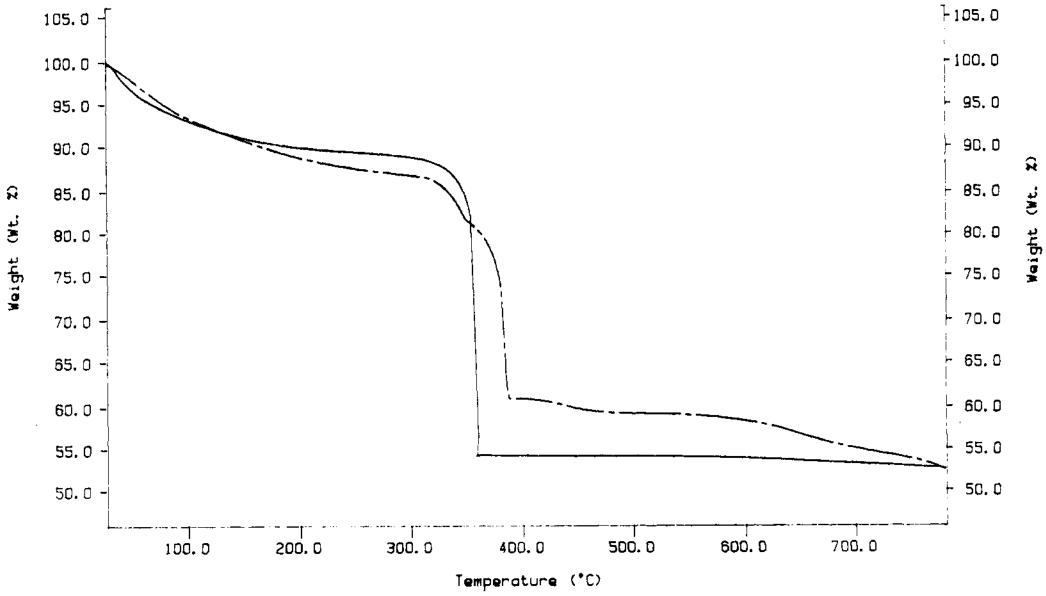

Figure 1. TGA data for the solid hydrolysis product of the reaction between $Ba(O_2CCMe_2OH)_2$ and Ti(O-*i*-Pr)$_4$ in pyridine showing the effects of heating in air (dashed line) versus O_2 (continuous line) atmospheres.

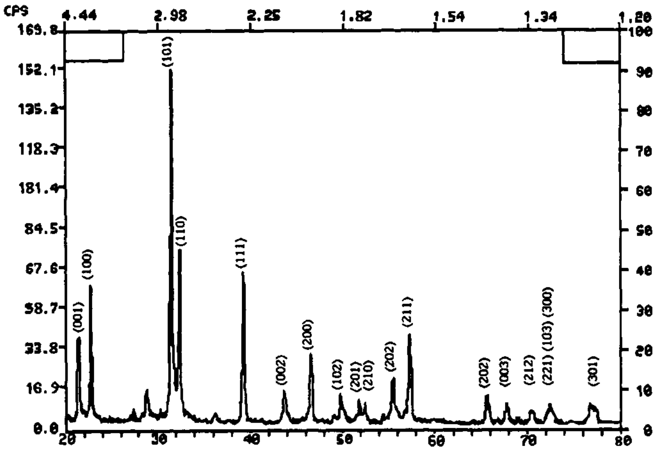

Figure 2. X-ray powder diffraction data for the $PbTiO_3$ formed from the reaction of $Pb(O_2CCMe_2OH)_2$ and Ti(O-*i*-Pr)$_4$ in pyridine followed by hydrolysis, removal of the volatile components in vacuo and thermolysis of the powder obtained at 350 °C in O_2. Peaks at 29° and 36° are due to the presence of a PbO impurity.

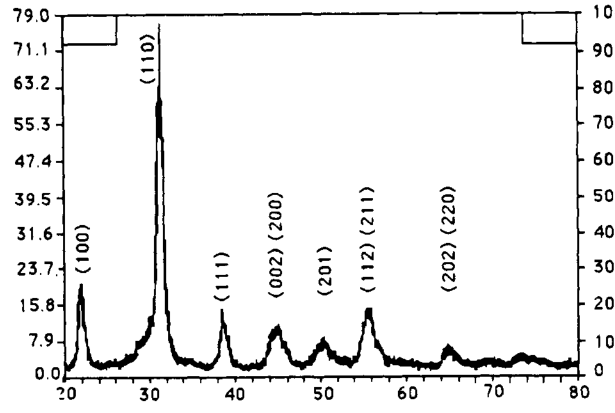

Figure 3. X-ray powder diffraction data for $PbZr_{0.52}Ti_{0.48}O_3$, see text for details.

strategy illustrated in Scheme I is successful for the formation of crystalline, complex integral and nonintegral metal oxides at relatively low temperatures and short reaction times. We are currently investigating the formation of thin films materials via this approach and the generality of these reactions to prepare other complex metal oxides.

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Registry No. $PbTiO_3$, 12060-00-3; $PbZrO_3$, 12060-01-4; $BaTiO_3$, 12047-27-7; $CaTiO_3$, 12049-50-2; $BaSnO_3$, 12009-18-6; lead titanium zirconium oxide, 106496-80-4; barium strontium titanium oxide, 116812-42-1.

Polymer Precursor Route to TiB_2/TiN Nanocomposites

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Because of their high melting points, hardness, and chemical resistance at high temperatures, metal borides and metal nitrides are two of the most important families of engineering ceramics.[3,4] We report in this communi-

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[3] For general reviews of the syntheses, structures and properties of metal borides see: (a) Greenwood, N. N.; Parish, R. V.; Thornton, P. *Q. Rev.* **1966**, *20*, 441–461. (b) Matkovich, V. I. *Boron and Refractory Borides*; Springer-Verlag: New York, 1977. (c) Post, B. In *Boron, Metallo-Boron Compounds and Boranes*; Adams, R. M., Ed.; Interscience: New York, 1964; pp 301–372. (d) Greenwood, N. N. *The Chemistry of Boron*; Pergamon: New York, 1975; pp 697–731. (e) Thompson, R. In *Progress in Boron Chemistry*; Pergamon: New York, 1970; Vol. 2, pp 173–230. (f) Hoard, J. L.; Hughes, R. E. In *The Chemistry of Boron and Its Compounds*; Muetterties, E. L., Ed.; Wiley: New York, 1967; pp 25–154.

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