

Synthesis and Characterization of Perovskite-phase Mixed-metal Oxides: Lead Titanate

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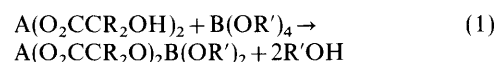
The reaction of $\text{Pb}(\text{O}_2\text{CCMe}_2\text{OH})_2$ and $(\text{acac})_2\text{Ti}(\text{OPr}^i)_2$, where $\text{acac} = \text{CH}_3\text{COCHCOCH}_3$, in a 1:1 stoichiometry results in elimination of two equivalents of HOPr^i and formation of a species with empirical formula $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2 \cdot x\text{C}_5\text{H}_5\text{N}]$. This species can act as a single-source precursor to PbTiO_3 . ^1H NMR studies of the formation of this species in pyridine reveal that the alkoxide ligands are completely eliminated and that the reaction appears to occur in two steps. The species $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2]$ does not react with HOPr^i , indicating that this reaction is irreversible. Thermolysis of $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2]$ results in loss of the organic ligands and the initial formation of amorphous material. Part of this amorphous material crystallizes at 310°C with 2 nm sized crystallites which can be attributed to the presence of either pyrochlore-phase PbTiO_3 or PbO , based on powder X-ray diffraction data. When the sample is heated further to 330°C , the remainder of the amorphous material starts to crystallize as perovskite-phase PbTiO_3 with a much larger crystallite size of 30 nm. X-Ray powder diffraction and transmission electron microscopy data are consistent with the presence of a small amount of 2 nm sized crystallites in perovskite-phase PbTiO_3 at 410°C . Analytical data (atomic absorption spectroscopy) were consistent with a 1:1 Pb:Ti atomic ratio, which we interpret as being more consistent with the presence of pyrochlore-phase PbTiO_3 than PbO . We believe that there is little or no phase transformation under these conditions. As a result we conclude that single-source precursors to PbTiO_3 result in lower crystallization temperatures than multiple sources of Pb and Ti and that pyrochlore-phase PbTiO_3 does not transform into crystalline perovskite-phase PbTiO_3 under these conditions.

There is increasing research interest in the chemistry of perovskite-phase mixed-metal oxide materials with the general formula ABO_3 , such as PbTiO_3 (PT), PbZrO_3 (PZ) and $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT), because they crystallize in polar space groups, giving rise to a variety of interesting physical properties.^{1–6} These properties include ferroelectric, piezoelectric and pyroelectric behaviour, which can be utilized in applications such as optoelectronic sensors, light detectors and mechanical transducers.^{6–10} Because the physical properties associated with the perovskite-phase are directly related to the intrinsic crystal chemistry of these materials, control over composition, homogeneity and crystallization behaviour is extremely important. For many applications it is necessary to synthesize pure, homogeneous crystalline materials, with the correct metal-atom stoichiometry.⁸ In order for these materials to be incorporated into existing solid-state devices, e.g. as thin films, low crystallization temperatures ($<400^\circ\text{C}$) are often desirable. However, a number of the technologically important ABO_3 phases are polymorphic and can crystallize with the non-polar pyrochlore structure, which does not exhibit ferroelectric, pyroelectric or piezoelectric properties.¹¹ Crystallization of the pyrochlore-phase in Pb-containing ABO_3 materials, rather than the perovskite-phase, is generally associated with Pb deficiency, which means that control of composition and stoichiometry is extremely important.¹²

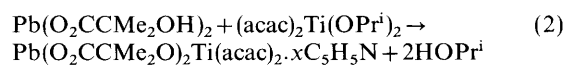
A large number of different approaches have been taken to synthesize perovskite-phase metal oxides. These methods include a variety of solid-, liquid- and gas-phase routes. The sol-gel route is popular because it allows for formation of either powders or films and has the capacity to control stoichiometry and homogeneity better than the other preparation methods.⁸ In general there are two main requirements for metal-organic solution routes to mixed-metal oxides: (1) the use of organic ligands that can be removed under mild conditions to give pure products and high ceramic yields and (2) a high level of mixing, preferably at the molecular level such that diffusional processes do not limit the crystallization temperature of the material. A typical solution route to a perovskite-phase material such as PbTiO_3 involves mixing

metal carboxylates, such as $\text{Pb}(\text{OAc})_2$, and metal alkoxides, such as $\text{Ti}(\text{OPr}^i)_4$, in alcohol solutions.^{8,12–16} After removal of the solvent, thermolysis of the intermediate generally requires crystallization temperatures of up to 500°C to yield either pyrochlore- or perovskite-phase mixed-metal oxides.¹² The high temperatures required for crystallization of the final product probably reflect the lack of control of the stoichiometry and homogeneity of the metals in the solution that result in diffusion-limited barriers to crystallization.

In order to determine if control over stoichiometry of the intermediate at the molecular level results in lower crystallization temperatures, we have prepared molecular intermediates that have a fixed metal A to metal B ratio in the ABO_3 system. In previous work, it has been shown that this method allows for the formation of crystalline, perovskite-phase mixed-metal oxide powders at relatively low temperatures ($300\text{--}400^\circ\text{C}$).^{17–19} The first step of this synthesis involves the reaction of a metal hydroxycarboxylate (glycolate) compound, e.g. $\text{Pb}(\text{O}_2\text{CCR}_2\text{OH})_2$, $\text{R} = \text{H}, \text{Me}$, with a metal alkoxide compound, e.g. $\text{Ti}(\text{OR}')_4$, $\text{R}' = \text{Pr}^i$, to form a mixed metal-organic intermediate with elimination of two equivalents of alcohol:



The second step involves the hydrolysis and/or thermolysis of the intermediate to form the final ABO_3 product. The thermolysis can be performed in air or oxygen-rich atmospheres. It has been reported previously that crystalline, perovskite-phase PbTiO_3 powders can be obtained on heating the intermediate to 350°C for 2 h. Here we report the results for a different single-source precursor that involves the reaction of $\text{Pb}(\text{O}_2\text{CCMe}_2\text{OH})_2$ with a modified metal alkoxide compound $(\text{acac})_2\text{Ti}(\text{OPr}^i)_2$ to form a mixed metal-organic intermediate:



The presence of acac in the coordination sphere of Ti improved the solubility of the intermediate and facilitated study of the formation of the intermediate by nuclear magnetic resonance (NMR) spectroscopy by providing a probe of the Ti centre and reducing the reactivity of the Ti moiety compared with the $\text{Ti}(\text{OPr}^i)_4$ species. In addition, the thermal decomposition and crystallization behaviour of this metal-organic intermediate was studied as a function of temperature and time.

Experimental

General Procedures

All reactions were conducted under an N_2 atmosphere employing standard Schlenk techniques.²⁰ The lead carbonate and titanium isopropoxide used in the formation of the precursors were purchased from J. T. Baker and Aldrich respectively. The lead precursor, $\text{Pb}(\text{O}_2\text{CCMe}_2\text{OH})_2$, was prepared by the reaction between lead carbonate and 2-hydroxyisobutyric acid in water as previously reported.^{18,19} The ^1H NMR spectroscopy was performed on a Bruker AC-250 in $[\text{D}_5\text{H}_5]$ pyridine using the protio impurity as an internal reference. Infrared (IR) spectroscopy was obtained in KBr pellets using a Perkin-Elmer 1600 series FTIR under N_2 . Elemental analyses were performed on a Perkin-Elmer 2400 elemental analyser in the Department of Chemistry at the University of New Mexico. Thermogravimetry (TG) was performed on a Perkin-Elmer 7700 thermogravimetric analyser. Transmission electron microscopy (TEM) with electron diffraction (ED) and energy-dispersive spectroscopy (EDS) were performed on a JEOL 2000-FX instrument operating at 200 keV. X-Ray powder diffraction data were collected on the PAD-V Scintag X-ray diffractometer using a modified top-mount technique. The *in situ* variable-temperature X-ray diffraction was performed on a Siemens D5000 θ/θ diffractometer using an Anton-Parr HTK hot stage with a platinum mount. Atomic absorption spectroscopy (AAS) for determination of lead was performed on a Perkin-Elmer 303 spectrophotometer with a 165 recorder in an acetylene-air mixture using the 283.3 nm wavelength line, slit = 4 (1 mm, 7 Å). Titanium was determined using an $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame with slit 3 (0.3 mm, 2 Å) and a wavelength of 364.3 nm. The samples were prepared as follows: 50 mg of sample was dissolved in 50% HNO_3 by warming below boiling for 2.5 h and then 5 cm^3 of concentrated HNO_3 was added. The samples were rinsed into 100 cm^3 volumetric flasks with 1% HNO_3 and then diluted to 100 cm^3 with H_2O . Then, 20 cm^3 aliquots were pipetted into dry 25 cm^3 volumetric flasks and 0.5 cm^3 of 30% H_2O_2 was added, mixed and allowed to stand for 10 min. Some of the samples were coloured. A blank (sample without H_2O_2) was run for each sample. The amounts of Pb and Ti were determined by AAS and the Ti content was confirmed by colorimetric analysis.²¹ In a control experiment, authentic PbTiO_3 was determined and found to give a Pb:Ti weight ratio of 0.23, the same as the calculated value for an atomic ratio of 1:1.

Synthesis

The compound $\text{Ti}(\text{OPr}^i)_4$, 0.2162 g, 0.76 mmol, was added to 0.156 g of acacH in *ca.* 30 cm^3 of pyridine ($\text{C}_5\text{H}_5\text{N}$) in a Schlenk flask. The mixture was added to lead dimethylglycolate (0.3143 g, 0.76 mmol) and stirred for a further 12 h. The solvent was removed *in vacuo* to give a golden, glassy powder with a yield of 96%. Attempts to recrystallize this material failed. Characterization data: $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2]$: ^1H NMR ($[\text{D}_5\text{H}_5]$ pyridine, 298 K, 250 MHz) δ : 1.66 {s, $[\text{O}_2\text{CC}(\text{CH}_3)_2\text{O}]_2$ }, 1.70 {s, $\text{CH}_3\text{COCHCOCH}_3$ }, 1.82

{s, $\text{CH}_3\text{COCHCOCH}_3$ }, 1.98 {s, $\text{CH}_3\text{COCHCOCH}_3$ }, 5.26 {s, $\text{CH}_3\text{COCHCOCH}_3$ }, 5.59 {s, $\text{CH}_3\text{COCHCOCH}_3$ }. IR (KBr pellet), ν/cm^{-1} : 2967 s, 2909 s, 2827 s, 1628 s, 1581 s, 1523 m, 1481 m, 1435 m, 1371 m, 1348 w, 1278 w, 1255 w, 1244 s, 1197 m, 1174 m, 1162 m, 1070 w, 1034 w, 1022 w, 987 m, 929 w, 900 w, 825 m, 778 w, 755 m, 709 m, 627 m, 604 s, 558 s. Calculated for $\text{PbTiC}_{18}\text{H}_{26}\text{O}_{10}$: C, 32.88; H, 5.32%; found: C, 32.39, H, 3.31%. Mp (dec) $\approx 180^\circ\text{C}$.

NMR-tube Reactions

In an NMR tube, 25 mg (0.0605 mmol) of $\text{Pb}(\text{O}_2\text{CCMe}_2\text{OH})_2$ was dissolved in a solution of 22 mg (0.0605 mmol) of $(\text{acac})_2\text{Ti}(\text{OPr}^i)_2$ in 0.5 cm^3 of $[\text{D}_5\text{H}_5]$ pyridine and the time recorded at the start of the reaction. The sample was transferred quickly to a thermally equilibrated NMR probe and an automation program was used to record the FIDs with variable delays. Similar reactions were carried out at various temperatures using the same method, and in some cases with additional reagents, such as HOPr^i .

Thermolysis Experiments

A modified tube furnace was used in these experiments. The furnace was fitted with an external thermocouple placed directly into the sample so that the furnace-heating cycle was controlled by the sample temperature and not the furnace temperature. This had the advantage of allowing us to measure and maintain the sample temperature precisely. Samples were removed at various times after heating to a given temperature or after heating for constant times and different temperatures. The crystallization behaviour of the samples was determined by X-ray powder diffraction and morphology and microcrystallinity were investigated by TEM.

Results and Discussion

The mixed metal-organic intermediate species $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2]$ was prepared by the reaction between $\text{Pb}(\text{O}_2\text{CCMe}_2\text{OH})_2$ and $(\text{acac})_2\text{Ti}(\text{OPr}^i)_2$ in pyridine according to eqn. (2). Combustion elemental analysis for C, H and N were variable depending on the length of time the samples had been exposed to vacuum drying. Occasionally N was observed together with a higher C and H content, which we attribute to the coordination of different amounts of pyridine to one of the metal centres. In these samples, ^1H NMR spectroscopy in C_6H_6 also revealed the presence of an amount of pyridine that was consistent with the combustion analytical data. AAS and colorimetric titration revealed a Pb:Ti weight ratio of 0.24, within the limits of experimental error of the calculated value, 0.23, for an atomic ratio of 1:1. Unfortunately, the solubility of this material in benzene and cyclohexane was too low to facilitate measurement of its molecular weight by freezing-point depression.

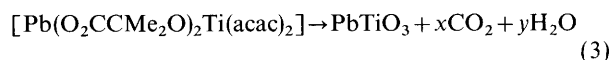
This species was further characterized by ^1H NMR spectroscopy in $[\text{D}_5\text{H}_5]$ pyridine. The spectrum of the isolated powder showed no evidence for the presence of isopropyl groups, consistent with complete elimination of the isopropoxide ligands and removal of isopropyl alcohol. The IR spectrum exhibited a band at 1628 cm^{-1} , consistent with the asymmetric $\nu(\text{C}=\text{O})$ stretch of a coordinated acetate ligand analogous to that observed in $\text{Pb}(\text{O}_2\text{CCMe}_2\text{OH})_2$. Other bands observed in the range $1600\text{--}1400\text{ cm}^{-1}$ were consistent with those expected for the presence of a bidentate chelated acac ligand.^{22–25} The absence of a $\nu(\text{O}-\text{H})$ band at *ca.* 3500 cm^{-1} also confirmed that the lead(n) glycolate OH groups had been consumed. Attempts to purify this material by recrystallization were unsuccessful owing to the lack of a suitable solvent. This

species requires a polar coordinating solvent that does not facilitate purification.

In order to provide more information on the reaction of $\text{Pb}(\text{O}_2\text{CCMe}_2\text{OH})_2$ with $(\text{acac})_2\text{Ti}(\text{OPr}^i)_2$, a series of time-dependent ^1H NMR studies were performed. A typical stacked plot of the methine region of the ^1H NMR spectrum of the reaction carried out at 23°C is shown in Fig. 1. In the methine region of the ^1H NMR spectrum, the resonances overlap too much to allow unambiguous interpretation. As the reaction progresses, the most obvious feature in the ^1H NMR spectra is the decreasing intensity of the isopropoxide methine septet resonance, labeled a, and the increasing intensity of the methine isopropyl alcohol septet resonance, b, with time. The intensity of the acac methine resonance, c, at δ 5.57 due to the starting material is smoothly reduced from the beginning of the experiment. Two new methine peaks emerge during the experiment, one at δ 5.3, d, at an early stage of the reaction and one at δ 5.6, e, ca. 70 min after the start of the reaction. We had hoped to determine quantitative kinetic parameters by repeating this reaction at different temperatures and integrating the areas under the resonances to determine the concentration at different times. However, the change in intensity of the isopropoxide and isopropyl alcohol methine resonances was different as a function of time and as a result it was not clear which peaks to use to monitor the rate of the reaction. Instead, some qualitative observations were made. A reaction was conducted in the presence of more than four equivalents of isopropyl alcohol. The overall rate of this reaction was ca. twice as large as that of the corresponding reaction between $\text{Pb}(\text{O}_2\text{CCMe}_2\text{OH})_2$ and $(\text{acac})_2\text{Ti}(\text{OPr}^i)_2$ without isopropyl alcohol at the same temperature. This suggests that the reaction is *not* an equilibrium process, and that the presence of isopropyl alcohol accelerates the reaction. To investigate the possibility of an equilibrium process further, the reaction of $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2]$ with six equivalents of isopropyl alcohol was investigated. The ^1H NMR spectra were monitored over a 24 h period and no isopropoxide resonance was observed, so it can be concluded that the reaction of eqn. (2) is irreversible. In the absence of a single-crystal X-ray diffraction study, these data do not establish conclusively whether the species $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2]$

contains both Ti and Pb in the same molecule (as is required for a single-source precursor). However, the data obtained thus far are consistent with the existence of a single species and so thermal decomposition of $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2]$ was studied in order to determine whether crystalline PbTiO_3 was formed and which phases were present.

The thermolysis of the $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2]$ intermediate was carried out in air and is proposed to occur according to eqn. (3).



The supposition that CO_2 and H_2O are the only reaction by-products is based on a previous observation that these were the only reaction by-products found on pyrolysis of an analogous compound, $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{OPr}^i)_2]$ in an O_2 atmosphere.²⁶ The weight loss of 53.9% calculated for formation of PbTiO_3 was consistent with the observed weight loss, 53.8%, determined by TG. The differential thermal analysis (DTA) shows two exothermic peaks at ca. 330 and 370°C . The peak at 370°C occurs with no concomitant weight loss and is consistent with the bulk crystallization of the sample.

A temperature-dependent X-ray diffraction study was carried out using a bulk sample of $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2]$, which was heated for 2 h in 20°C increments from 310 to 450°C in order to investigate the crystallization behaviour. The *ex situ* X-ray diffraction data for different temperatures are shown in Fig. 2. At 310°C , a broad peak with a maximum at ca. $2\theta = 28^\circ$ was observed. It is difficult to assign this broad peak to a particular phase with these limited data, but this d -spacing is consistent with the (222) and (311) lattice planes of pyrochlore-phase PbTiO_3 (JCPDS file number 26-0142), the (101) lattice plane of litharge (JCPDS file number 5-0561) and the (111) lattice plane of massicot (JCPDS file number 38,1477). TEM data revealed the presence of a porous, amorphous (by ED) material. EDS, AAS and colorimetric titration revealed a Pb:Ti atomic ratio of 1:1 within the limits of experimental error. However, there were some variations in the EDS data: titanium-rich areas were observed as well as areas of atomic ratio 1:1, Pb:Ti. In the areas that we examined, we did not observe any lead-rich areas. Based on

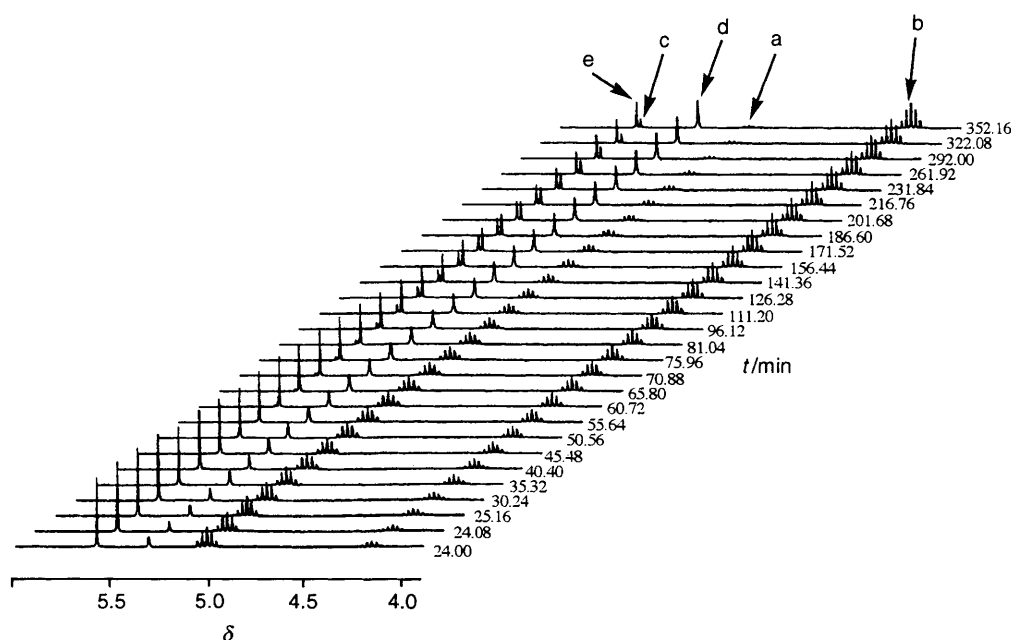


Fig. 1 Methine region of the acac and isopropoxide ligands in the kinetic study of the reaction of $\text{Pb}(\text{O}_2\text{CCMe}_2\text{OH})_2$ with $(\text{acac})_2\text{Ti}(\text{OPr}^i)_2$ as a function of time

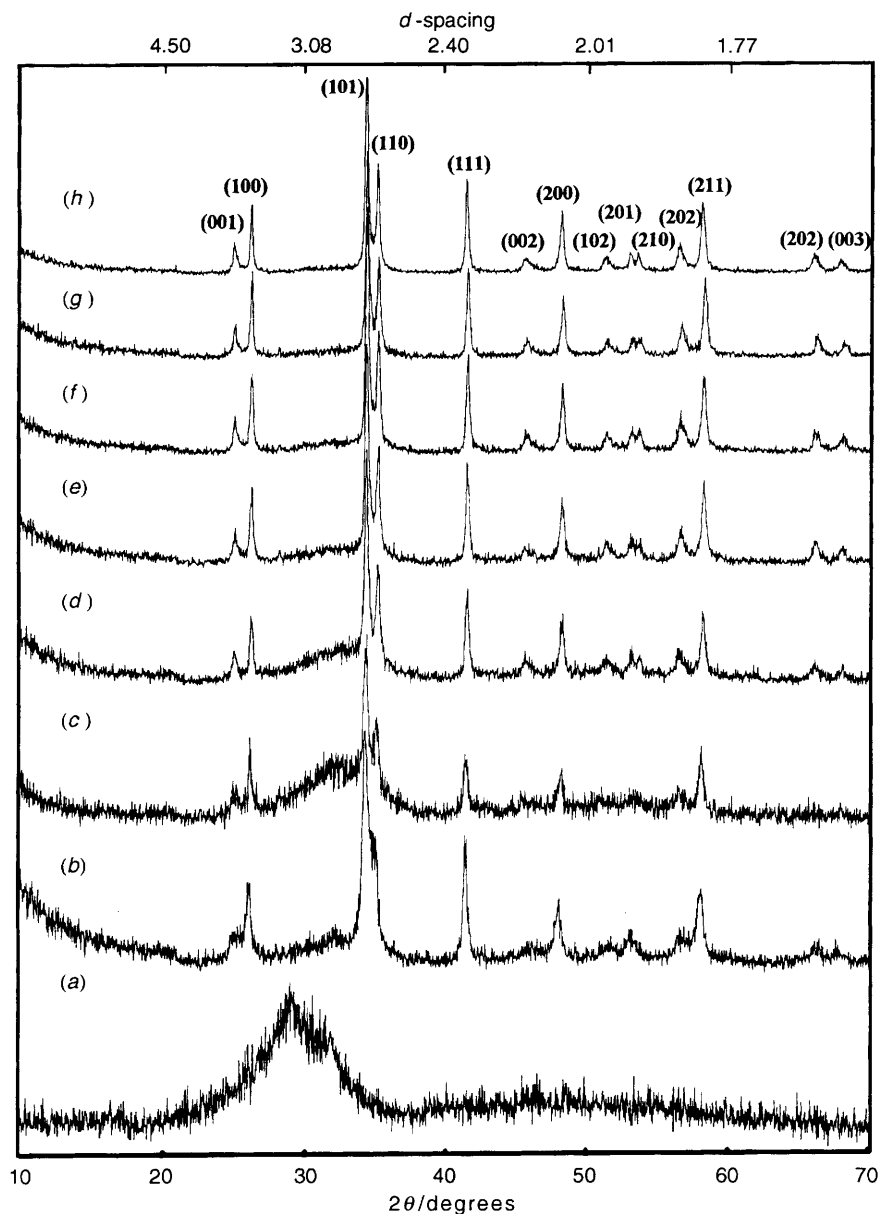


Fig. 2 Variable temperature *ex situ* powder X-ray diffraction of the thermolysis product of $\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2$. $T/^\circ\text{C}$: (a) 310, (b) 330, (c) 350, (d) 370, (e) 390, (f) 410, (g) 430, (h) 450.

these observations, we suspect that the broad peaks are most likely derived from pyrochlore-phase PbTiO_3 rather than PbO , but this distinction is difficult to make conclusively based on these data. This highlights one of the problems associated with the use of EDS as a probe of compositional uniformity, which is the small sample area of the electron beam (*ca.* $0.03\ \mu\text{m}^2$). Therefore these data may not be representative of the composition of the bulk sample. It is also possible that the sample examined did not contain any of the lead-rich regions due to the small sample size used for TEM measurements. A second bulk analytical technique, such as AAS, should be employed to investigate the composition of the bulk sample.

When the sample was heated further, the peaks characteristic of the perovskite-phase PbTiO_3 appeared with no apparent growth in the size of the crystallites derived from the broad peak at $2\theta = 28^\circ$. Continued heating to 450°C developed the perovskite structure. The size of the perovskite crystallites and crystallites due to the second phase was estimated from a line-broadening analysis using the Scherrer equation. The

size of the perovskite crystallites after heating the sample to 410°C for 16 h was determined to be *ca.* 30 nm. The width of the peak at $2\theta = 28^\circ$ was consistent with a crystallite size of *ca.* 2 nm at 310°C . Since X-ray powder diffraction is a bulk sample characterization technique, it is not clear whether the phase responsible for the broad peak has been converted to perovskite at high temperatures or whether the broad peak is simply obscured. AAS and colorimetric titration revealed a Pb:Ti atomic ratio of 1:1 in this material, more consistent with the presence of the pyrochlore-phase PbTiO_3 than a phase of PbO .

In order to investigate the microstructure and phase segregation in this system further, the sample was investigated by TEM. Fig. 3 and 4 show TEM photographs at two different magnifications of the material obtained after heating to 410°C . Fig. 3 shows the presence of large, *ca.* 30 nm crystallites, which we believe are due to perovskite-phase material, and other smaller features on the crystallite edges with dimensions of *ca.* 2 nm. These dimensions are consistent with the line broadening observed by X-ray diffraction and we assign the

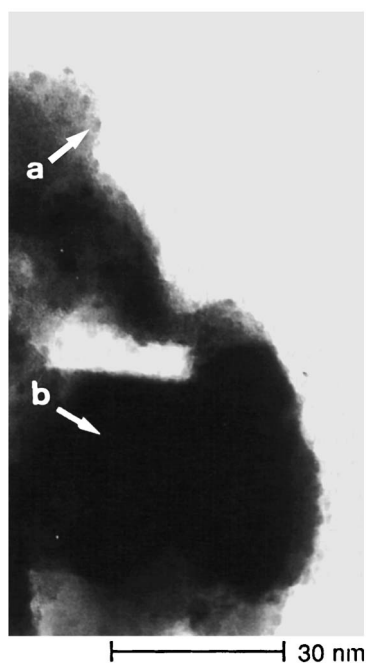


Fig. 3 Transmission electron micrograph of PbTiO_3 annealed at 410°C showing (a) 2 nm and (b) 30 nm crystallites

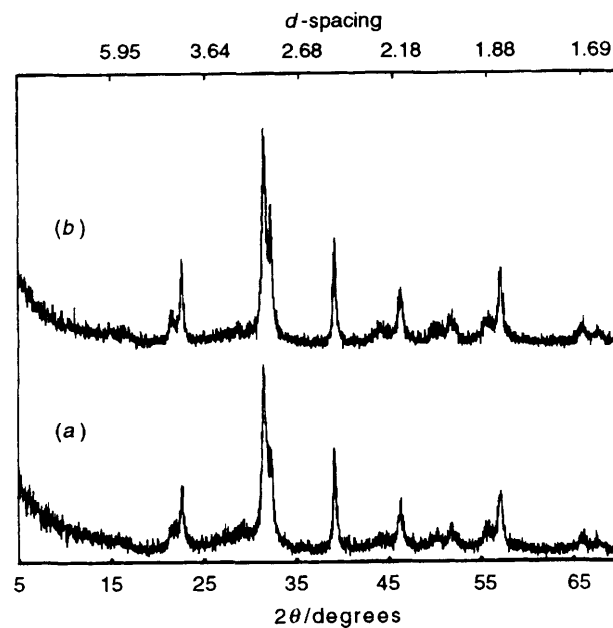


Fig. 5 Variable-time powder X-ray diffraction of the thermolysis product of $\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2$ at 330°C : (a) 2 h, (b) 48 h



Fig. 4 Transmission electron micrograph of PbTiO_3 annealed at 410°C showing a 30 nm perovskite crystallite and emphasizing the lattice fringes

smaller features to the crystallites attributed to the peak at $2\theta = 28^\circ$. In Fig. 4, a crystallite *ca.* 30 nm in size is clearly visible that exhibits diffraction fringes with a *d*-spacing of *ca.* 3 Å, which corresponds to the (101) plane of perovskite-phase, PbTiO_3 . As a result of these observations, we believe that the perovskite-phase crystallites grow from amorphous ' PbTiO_3 ' at a significantly faster rate relative to the second phase, which we believe is pyrochlore. Based on TEM data it also appears that the majority of the sample is crystalline.

To examine whether the second phase grows with time, two thermal annealing experiments were performed at constant temperature, 330°C , and two different times, 2 h and 48 h, see Fig. 5. The data obtained after heating the sample for 2 h is similar to that shown in Fig. 2, showing the presence of both the broad peak and the perovskite-phase. Only the perovskite-phase PbTiO_3 was observed to grow after 48 h and the lines had sharpened slightly indicating a small increase in crystallite size. The peaks due to the second phase were observed to be similar in size as for the sample heated for 2 h. Another series of X-ray powder diffraction experiments was carried out where $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2]$ was heated at a constant tem-

perature of 410°C for periods of between 2 and 32 h. Fig. 6 shows that there is little change in crystallite size after heating the sample for longer than 2 h. Furthermore, X-ray powder diffraction data obtained after heating $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2]$ in air at 410°C for 10 min showed that the crystallization is essentially complete after this time. From these data, we infer that this mixed-metal intermediate decomposes rapidly at 330°C and above to form mainly perovskite-phase PbTiO_3 .

The same variable-temperature X-ray powder diffraction experiment as presented in Fig. 2 (330 – 450°C) was repeated *in situ*. The sample was heated using the same parameters as in the *ex situ* study. The two major differences were that the X-ray data was now obtained at elevated temperatures and that the sample size was much smaller than the *ex situ* experiment. These data are shown in Fig. 7. Note that peaks consistent with the crystallization of perovskite-phase PbTiO_3 are not visible until 390°C , probably due to the small size of the sample being heated. In the *ex situ* variable-temperature X-ray diffraction experiment, the bulk sample may crystallize differently owing to the exothermic nature of the reaction (as shown by the DTA data). The final product formed at 450°C

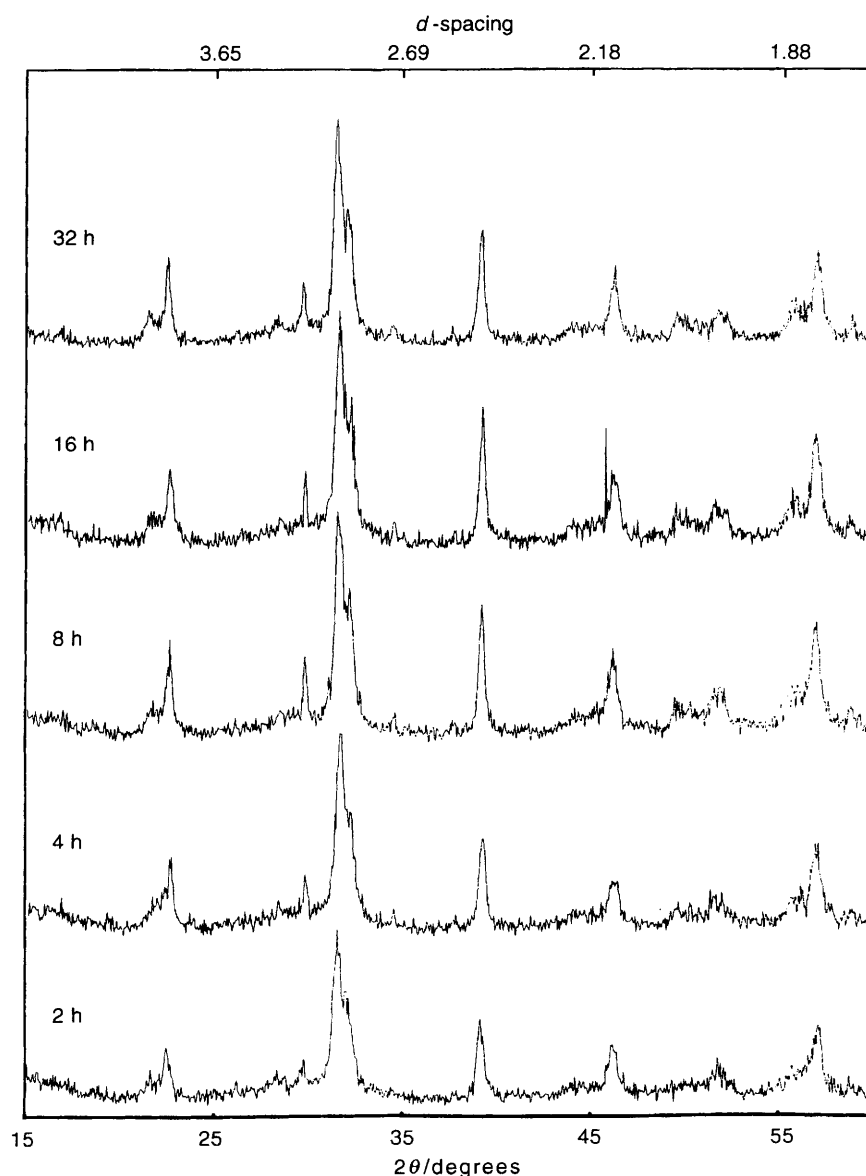


Fig. 6 Variable-time powder X-ray diffraction of the thermolysis product of $\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2$ at 410°C

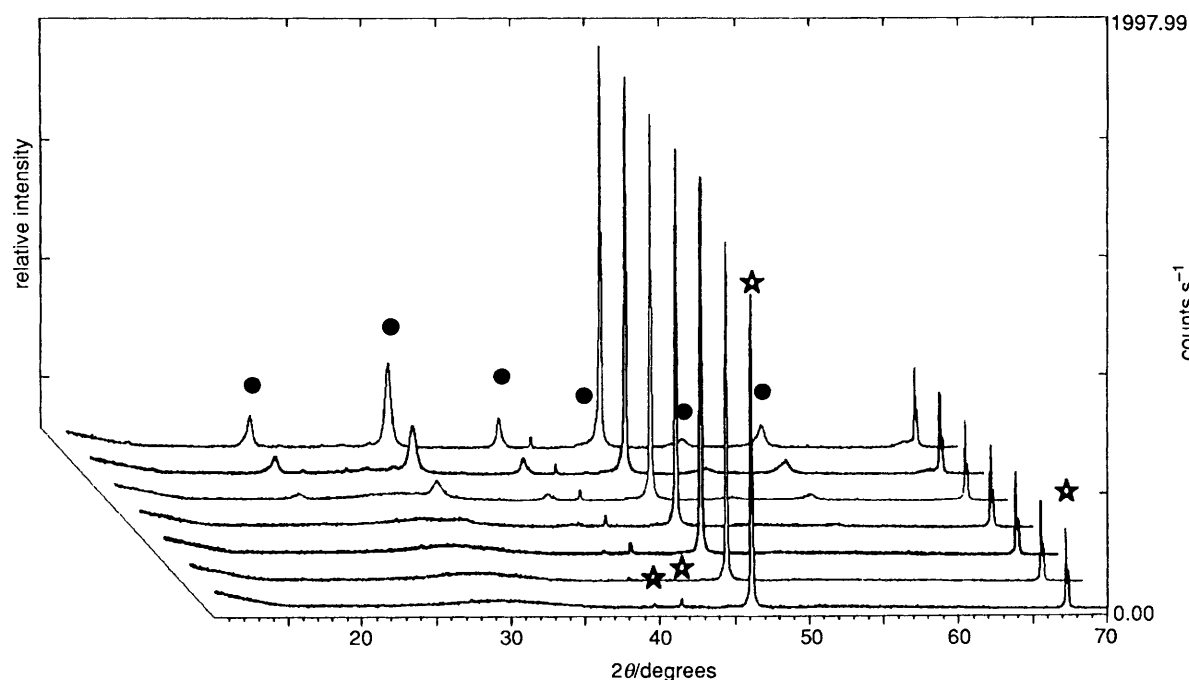


Fig. 7 Variable-temperature *in situ* powder X-ray diffraction of the thermolysis product of $\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2$. The peaks labelled * are derived from the platinum heating strip and the peaks labelled ● are associated with cubic, perovskite-phase PbTiO_3 .

is cubic, perovskite-phase PbTiO_3 , not the tetragonal phase observed in the *ex situ* study, consistent with the phase diagram for PbTiO_3 .

Conclusions

The reaction of $\text{Pb}(\text{O}_2\text{CCMe}_2\text{OH})_2$ with $(\text{acac})\text{Ti}(\text{OPr}^i)_2$ in pyridine gives a product consistent with the empirical formula $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2 \cdot x\text{C}_5\text{H}_5\text{N}]$. ^1H NMR studies of the formation of this species in pyridine reveal that the alkoxide ligands are completely eliminated and that the reaction appears to occur in two steps. The species $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2 \cdot x\text{C}_5\text{H}_5\text{N}]$ does not react with HOPr^i , indicating that the reaction of eqn. (2) is irreversible. The molecular identity of $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2]$ was not established in this study but, based on its reactivity, it is believed to be a single species.

Thermolysis of the organic ligands of $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{acac})_2 \cdot x\text{C}_5\text{H}_5\text{N}]$ below 310°C results in formation of amorphous ' PbTiO_3 '. When the sample is heated to 310°C part of this amorphous material crystallizes to form a phase composed of 2 nm sized crystallites with $2\theta = 28^\circ$ that could not be unambiguously identified, but is consistent with either pyrochlore-phase PbTiO_3 or PbO . On further heating to 330°C , it appears that the remainder of the amorphous material starts to crystallize as perovskite-phase PbTiO_3 with a much larger crystallite size of 30 nm. X-Ray powder diffraction and TEM data revealed that the phase that gave rise to the broad peaks in the X-ray diffraction was still present at 410°C . Analytical data tended to support the assignment of the broad peaks to pyrochlore-phase PbTiO_3 rather than PbO , but the data are not unambiguous. As a result we believe that there is little or no phase transformation from the second phase (possibly pyrochlore) to perovskite under these conditions. We conclude that in designing metal-organic routes to crystalline perovskite-phase PbTiO_3 at low temperatures, pyrochlore PbTiO_3 formation is undesirable because the pyrochlore to perovskite-phase transition is slow under these conditions.

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