Journal of the European Ceramic Society **19** (1999) 1345–1348
PII: S0955-2219(98)00431-2

Effect of Precursor Type on the Microstructure of $PbTiO_3$ Thin Films

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Abstract

Lead–titanium solution precursors were prepared by (i) preceding syntheses of the lead precursor by reaction of lead acetate with 2-methoxyethanol and titanium methoxyethoxide and their subsequent reaction, (ii) reaction between anhydrous lead acetate and titanium methoxyethoxide, (iii) reaction between lead oxide and titanium methoxyethoxide in 2-methoxyethanol as a common solvent. The lead acetate-derived precursor exhibits a complex thermal decomposition with the highest weight loss, while smooth pyrolysis with the lowest weight loss characterises the lead-oxide-derived precursor. Variations in precursor structure affect the pyrolysis behaviour, thickness and microstructure of as-deposited lead titanate thin films. © 1999 Elsevier Science Limited. All rights reserved

Keywords: $PbTiO_3$, precursors-organic, sol–gel processes, films, microstructure-final.

1 Introduction

Solution deposition of ferroelectric thin films is a promising way to obtain precise stoichiometric control of complex mixed oxide compositions such as lead titanate (PT) or lead zirconate titanate solid solution (PZT). In the widely used 2-methoxyethanol based route introduced by Gurkovich[1] and Budd,[2] variations in microstructures of PZT thin films and hence in their functional response are achieved although the same starting compounds are used.[3,4] Coffman *et al.*[5] showed that differences in the synthesis conditions, amount of hydrolysis water and type of catalysis influence the pyrolysis of PZT precursors and the microstructure of the thin films.

In this work various solution precursors were prepared following the 2-methoxyethanol route[1,2] to deposit thin films. $PbTiO_3$ was chosen as a model compound for PZT solid solution. The following lead sources were used: the lead precursor obtained by repeated distillation of anhydrous lead acetate in 2-methoxyethanol, anhydrous lead acetate and lead oxide. The latter had been successfully introduced into PZT processing by Kosec *et al.*[6] To avoid transalcoholysis titanium butoxide was separately reacted with 2-methoxyethanol to yield methoxyethoxide. Quantitative ^1H NMR, FTIR and thermal analysis with mass spectrometry of the evolved species were used to deduce the functional group content of the precursors. In this way, the correlation between the lead–titanium precursor structure and the microstructure of thin films could be drawn.

2 Experimental

The manipulation of chemicals and reactions were performed in a dry argon atmosphere using standard Schlenk techniques.[7] The metal content of anhydrous lead acetate and titanium alkoxide was determined gravimetrically.

First, 0·05 mole of $Pb(OAc)_2$ was dissolved in 2-methoxyethanol. The 0·5 M solution was distilled first at normal pressure and then *in vacuo* (< 1 mbar). After diluting the procedure was repeated five times, yielding a brownish solid product denoted as the lead precursor.

Also 0·05 mole of $Ti(OnBu)_4$ was diluted in 2-methoxyethanol to obtain a 0·5 M solution and distilled at a reduced pressure of 260 mbar. The distillation was repeated three times.

Batches of lead–titanium (PT) precursors (0·5 M, 25 ml) with a Pb/Ti ratio of 1·1/1 were prepared by dissolving (i) lead precursor, (ii) lead acetate and (iii) lead oxide in titanium methoxyethoxide/2-methoxyethanol solution. The first two solutions

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were distilled at 123°C to remove the by-product 2-methoxyethylacetate[8] and again rediluted to 0·5 M. Solution (iii) was heated to 121°C and kept at that temperature for 30 min. 4 vol% formamide was added to the sols as drying-control additive.[9]

Thin films were deposited on platinized silicon substrates (150 nm Pt/50 nm TiO_2/Si) by spin-coating, pyrolysed at 350°C for 1 min on a hot plate and annealed in air at 600°C for 15 min at a heating rate of 450°C min^{-1}. The pyrolysis conditions were determined on the basis of preceding DSC analysis of as-deposited thin films.

Lead and titanium precursors dissolved/diluted in deuterated chlorophorm were analysed by ^{1}H NMR with acetonitrile as internal standard. Lead precursor diluted with KBr or poly-oil was analysed by FTIR.

Thermal decompositions of lead-titanium presursors dried at 60°C were analyzed by thermogravimatric analysis with mass spectrometry of evolved gases (TG/EGA) at a heating rate of 10°C/minute in flowing air.

The thickness of as-pyrolysed and as-annealed films was determined by profilometer. As-annealed films were characterised by scanning electron microscope. Grain size was determined by the linear intercept method.

3 Results and Discussion

Lead acetate can in principle react with 2-methoxyethanol to yield lead 2-methoxyethoxide [eqn (1)]. However according to the literature the reaction is not complete, with some acetate groups still remaining in the product.[8,10]

$$\begin{aligned}&Pb(CH_3COO)_2 + 2CH_3OCH_2CH_2OH \rightarrow\\&Pb(CH_3OCH_2CH_2O)_2 + CH_3COOH\end{aligned} \tag{1}$$

From NMR results of successive distillation residues the acetate/2-methoxyethyl ratio decreases from 1·67 after the first distillation to 0·73 after the second one, 0·19 after the fifth one and does not change noticeably afterwards. The sixth product with an acetate/2-methoxyethyl ratio of 0·17 was used afterwards as lead precursor.

FTIR analysis of lead precursor confirmed the presence of acetate groups (bands at 1550 and 1370 cm^{-1}) and hydroxyl groups at 3380 cm^{-1}. The latter probably stem from the esterification between the acetic acid released and 2-methoxyethanol.[5,8] The amount of water was not determined.

In the case of the titanium precursor, according to NMR results complete exchange of butyl with 2-methoxyethyl groups is achieved only after three successive distillations.

Lead titanium precursors were prepared from lead precursor, lead acetate or lead oxide, and titanium 2-methoxyethoxide and are denoted hereafter as PT-synth., PT-ac. and PT-ox. The simplest precursor PT-ox. should contain only oxo and 2-methoxyethoxide ligands, while in the case of PT-synth. 2-methoxyethoxide ligands should prevail. In synthesis of PT-ac. the distillation step was intentionally performed at ambient pressure, to obtain a product comparable to literature reports containing both alkoxide and acetate groups.

Thermal analysis was used to study the functional group contents of the precursors and the results are shown in Fig. 1.

As expected, PT-ox. has the lowest weight loss of 12·7%. The sample loses 2·5% weight upon heating to 200°C, 1% from 200 to 300°C, 1% from 300 to 380°C and further 8·2% from 380 to 480°C. The weight loss below 200°C is accompanied by the evolution of water and those above 200°C by the evolution of water and carbon dioxide as determined by mass spectrometry [Fig. 1(a)].

PT-synth. loses 18·2% weight. Upon heating to 200°C the sample loses 4·5% water. In addition traces of acetone (10^{-4} lower signal than those of water and carbon dioxide) were found. From 200 to 300°C and from 300 to 440°C weight losses of 5·5 and 4%, respectively, were determined. Water, carbon dioxide and traces of acetone are evolved. The sample loses a further 4·2% weight up to 520°C with the evolution of carbon dioxide and water [Fig. 1(b)].

Acetone (CH_3COCH_3) together with carbon dioxide is a side product of acetate group decomposition [eqns (2) and (3)].[5]

$$2CH_3COO^- \rightarrow CO_3^{2-} + CH_3COCH_3 \tag{2}$$

$$CO_3^{2-} \rightarrow CO_2 + O^{2-} \tag{3}$$

PT-ac. exhibits the highest weight loss of 22·5%. Up to 220°C there is a weight loss of 9·5% due to evolution of water. From 220 to 320°C the weight loss of 7% and from 320 to 400°C that of 4% is due to evolution of water, carbon dioxide and acetone. The sample loses a further 2% up to 510°C with the evolution of carbon dioxide and water [Fig. 1(c)].

With the exception of traces of acetone in PT-synth PT-ox and PT-synth have rather similar decomposition products although in different amounts, water up to 200°C and water and carbon dioxide in three further steps upon further heating. The former is evolved by desorption while the latter are side products of condensation reactions.[5] We assume that the rather high amount of carbon dioxide with respect to water at about 500°C stems from carbonaceous residues.

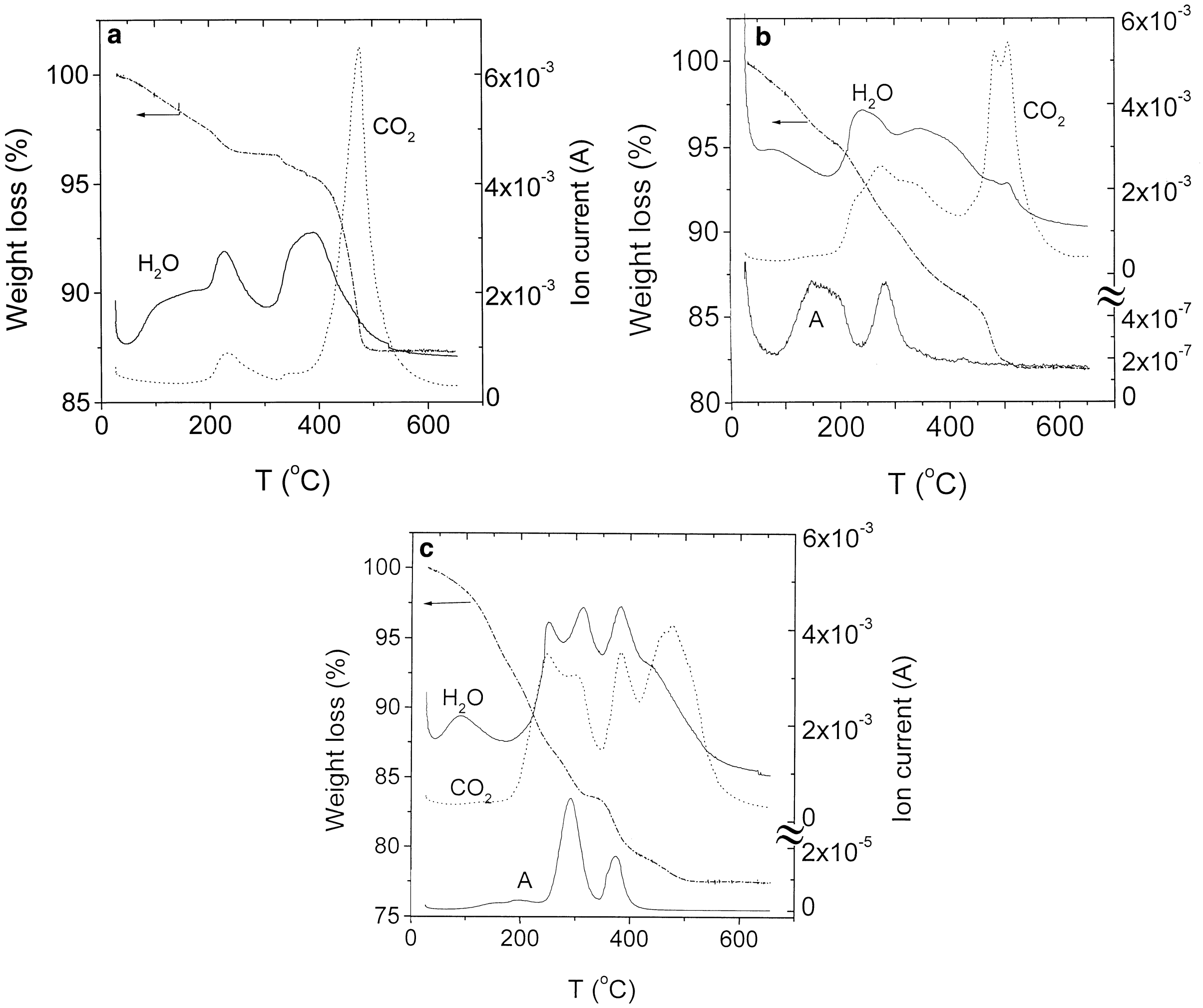

Fig. 1. Thermogravimetric and dynamic mass spectrometric curves of (a) PT-ox., (b) PT-synth., (c) PT-ac precursors, dried at 60°C. The following mass peaks are shown: 18 (H_2O), 44 (CO_2), 58 (acetone, A). Note that split graphs (lower part) in (b) and (c) represent the MS curves of acetone at 10^{-2} and 10^{-4} times lower ion current, respectively, compared to the values for H_2O and CO_2.

PT-ac. has a complex and quite different decomposition pathway above 200°C, consisting of four major weight loss steps. In addition to water and carbon dioxide a small amount of acetone is evolved (10^{-2} lower signal), confirming the presence of acetate groups in the precursor.[5] One should note that traces of acetone found upon decomposition of PT-synth. confirm the presence of residual acetate groups in that sample.

The thickness of as-pyrolyzed and as-annealed PT films was determined (Table 1). PT-ac. thin films have the lowest and PT-ox. the highest thickness values both after pyrolysis and annealing; the values ranging from 285 to 415 nm after pyrolysis and from 270 to 395 nm after annealing. The film thicknesses are in inverse proportion to the weight losses of the respective precursors. It should also be mentioned that the viscosities of all PT sols were essentially the same, in the range 2·6–2·7 mPas.

Shrinkage of PT-synth., PT-ac. and PT-ox thin films is 8·3, 5·3 and 4·8%, respectively. We interpret the different values of shrinkage as resulting from the various polymeric structures of PT precursors undergoing processes of rearrangement and skeletal densification upon thermal treatment.[5]

The microstructures of PT thin film surfaces annealed at 600°C for 15 min are shown in Fig. 2. The average grain size expressed as a linear intercept equals to 100, 85 and 75 nm for PT-synth., PT-ac. and PT-ox., respectively (Table 1). Comparing only PT-synth. and PT-ox. with prevailing alkoxide groups there is a relation between the microstructure and precursor structure. With a higher organic group content i.e. a more 'diluted' starting polymeric network, fewer nuclei are formed leading to a larger average grain size and vice versa, a lower organic group content promotes a smaller grain size. For PT-ac., characterised by a high

Table 1. Thickness of PT thin films after pyrolysis at 350°C for 1 min and after annealing at 600°C for 15 min, corresponding shrinkage and grain sizes expressed as average linear intercepts (L_3) of thin films annealed at 600°C for 15 min. The thickness values are the average of three measurements

Thin film	$d_{pyro.}$ *(nm)*	$d_{anneal.}$ *(nm)*	*Shrinkage (%)*	L_3 *(nm)*
PT-synth.	360	330	8·3	100
PT-ac.	285	270	5·3	85
PT-ox.	415	395	4·8	75

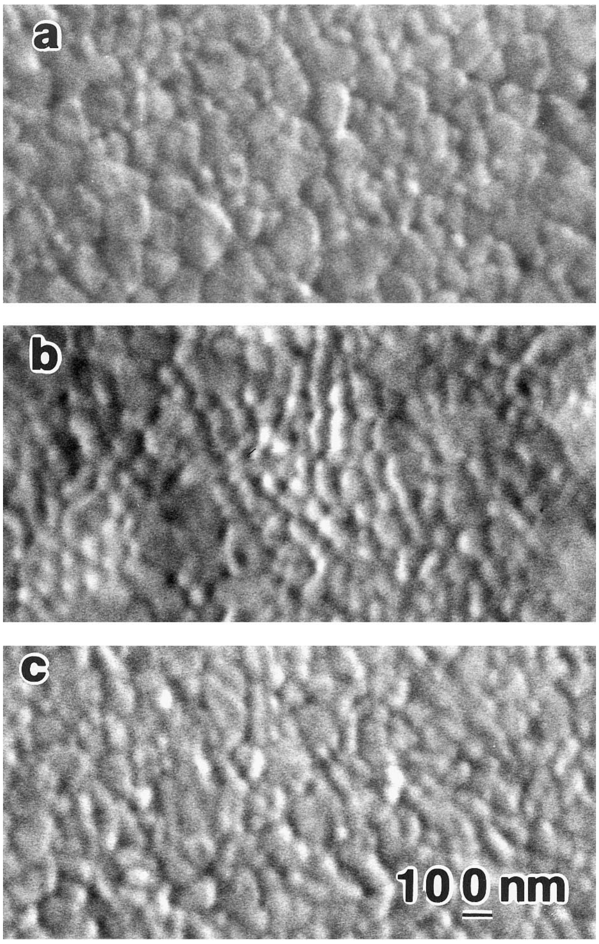

Fig. 2. Microstructures of (a) PT-synth., (b) PT-ac., (c) PT-ox. thin films (surface), annealed at 600°C for 15 min.

organics content and complex pyrolysis, we assume a different pathway of nucleation and growth of perovskite grains.

4 Summary

Lead titanium precursors were prepared from various lead sources, i.e. as-synthesized lead precursor, lead acetate and lead oxide, and titanium 2-methoxyethoxide in 2-methoxyethanol. It was found that the functional group content of the solution precursors affects the thermal decomposition, shrinkage and grain size of the as-deposited thin films.

Acknowledgements

Support by the Ministry of Science and Technology of the Republic of Slovenia within the National Research Programme is acknowledged. The authors thank Mrs Jana Cilenšek and Mr Zoran Samardžija for experimental assistance.

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