Scientific Paper

Crystallization Study of the Alkoxide-Based $Pb(Zr_{0.30}Ti_{0.70})O_3$ Thin-Film Precursor[†]

Barbara Malič, Jena Cilenšek, Mira Mandeljc, and Marija Kosec

Institut Jožef Stefan, Jamova 39, 1000 Ljubljana, Slovenija
Barbara.malic@ijs.si

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[†] Dedicated to the memory of Prof. Dr. Tatjana Malavašič

Abstract

Thermal decomposition and crystallization of the alkoxide-based precursor for $Pb(Zr_{0.30}Ti_{0.70})O_3$ thin films by chemical solution deposition (CSD) method is studied by a combination of thermal analysis methods and X-ray diffraction. The precursor was prepared from lead oxide and zirconium and titanium n-butoxides in 2-methoxyethanol and dried at 60 °C. Thermal decomposition takes place stepwise: solvent evaporation is followed by the organic-group decomposition between 200 and 440 °C, carbonate-group removal and crystallization between 440 and 600 °C. The crystallization of the thermodynamically stable perovskite phase that occurs through the transitory pyrochlore-type phase, was followed by differential thermal analysis; in this case the sample was precedingly heated at 400 °C. The crystallization of the perovskite phase is exothermic, with enthalpy equal to 33 kJ/mol.

In the case of the $Pb(Zr_{0.30}Ti_{0.70})O_3$ thin film deposited on Pt(111)/Si substrate the crystallization temperature of the perovskite phase is further decreased as a consequence of the heterogeneous nucleation on the platinum surface: pure perovskite phase is obtained at as low as 400 °C. The crystallization of (111) oriented perovskite phase occurs directly from the amorphous phase.

Key words: $Pb(Zr_{0.30}Ti_{0.70})O_3$, alkoxide, thin films, thermal analysis, crystallization

Introduction

Research on chemical solution deposition (CSD) methods for $Pb(Zr,Ti)O_3$ (PZT) ferroelectric thin films is oriented towards higher reliability and lower processing temperatures.[1–3] The 2-methoxyethanol based route, originally used by Gurkovich and Blum[4] in case of powders and Budd, Dey and Payne[5] for thin films is probably the most widely spread method of CSD. It is based on the reactions of transition metal alkoxides $TM(OR)_4$ (TM = Zr, Ti) with soluble lead compounds, such as acetate, in 2-methoxyethanol resulting in stable oligomeric or polymeric sols. The reaction between an alkoxide and an acetate ($Pb(OAc)_2$, OAc-: CH_3COO-) can proceed by either ester elimination (Eq. 1) and/or addition (Eq. 2, in this case the coordination number of the transition metal is increased) leading to the formation of oxo or acetate bridges between the metals.[6–10]

$$\text{-[Pb-OAc] + [RO-M]-} \rightarrow \text{-[Pb-O-M]- + ROAc} \qquad (1)$$

$$\text{-[Pb-OAc] + [RO-M]-} \rightarrow \text{-[Pb-OAc}\rightarrow\text{M-OR]-} \qquad (2)$$

Kosec and coworkers[11,12] introduced lead oxide as the lead source. Although it is not soluble in the 2-methoxyethanol, it is dissolved upon heating in a solution of titanium and zirconium alkoxides according to the proposed reaction (Eq. 3)

$$\text{PbO + [RO-M]-} \rightarrow \text{-[Pb-O}\rightarrow\text{M-OR]-} \qquad (3)$$

The following steps of CSD include the deposition of the sol on a substrate, typically platinized silicon, by spin-coating, drying, pyrolysis and crystallization.[1–3]

Solution-based synthesis of a heterometallic precursor enables higher homogeneity in comparison to solid-state synthesis and markedly lower formation temperature of the target complex oxide material. In case of thin films the temperature of crystallization is further reduced due to the heterogeneous nucleation on a suitable substrate, in case of $Pb(Zr,Ti)O_3$ mostly platinized silicon.[13–15] Thus crystalline $Pb(Zr,Ti)O_3$ deposited on platinized silicon substrate is obtained at as low as 400 °C.[16]

The aim of the present work was to study the thermal decomposition and crystallization of the heterometallic precursor for $Pb(Zr_{0.30}Ti_{0.70})O_3$ thin films prepared by the 2-methoxyethanol based route with lead oxide as the lead-source, by combination of thermal analysis and X-ray diffraction. These results were further linked to the study of low-temperature crystallization of the $Pb(Zr_{0.30}Ti_{0.70})O_3$ thin films on platinized silicon.

Experimental

The sols corresponding to the composition of $PbZr_{0.30}Ti_{0.70}O_3$ with 10 mol% PbO excess, further denoted as PZT, were prepared in 100 ml batches by diluting zirconium and titanium n-butoxides ($Zr(OC_4H_9)_4$, $Ti(OC_4H_9)_4$) in 2-methoxyethanol (CH_3-O-C_2H_4-OH) and by adding lead oxide (PbO) in the required quantity. The metal contents of the alkoxides were determined gravimetrically. The reaction mixtures were heated to approximately 100 °C to get clear solutions. After 2 hours of refluxing and distillation of the by-products, stable 0.5 M sols were obtained. All manipulations were performed in dry nitrogen atmosphere.

PZT thin films were deposited on $Pt/TiO_2/SiO_2/Si$ substrates (Aixacct) by spin-coating at 3000 rpm for 30 seconds and dried at 200 °C for 2 minutes on a hot plate. The procedure was repeated 4 times to obtain the thickness of about 250 nm. The films were further heated at 350, 375 and 400 °C for 30 minutes on a hot plate.

The thermal decomposition of the sols, dried at 60 °C, was followed by simultaneous thermal analysis (thermogravimetry and differential thermal analysis TG/DTA, Netzsch STA 409, coupled with a mass spectrometer, Balzers Thermostar GSD 300D, for the analysis of evolved gases (EGA), heating rate 10 °C/min., flowing air atmosphere, Pt crucibles).

To determine the enthalpy of crystallization by differential thermal analysis, the as-dried sample was further thermally treated for 5 hours at 400 °C to remove the organic groups but to keep it in amorphous state in agreement with the procedure of Schwartz and Payne.[17] The analyses were performed in platinum pans with the heating rate of 10 °C/min. The results are the average of three measurements.

We calculated the enthalpy of crystallization according to Eq. 4.[18]

$$\Delta H = K \cdot A \cdot M \qquad (4)$$

Δ H: enthalpy (J/mol)

K: calibration coefficient (J/Vs)

A: DTA peak area (Vs/g)

M: molar mass (g/mol)

The calibration coefficient of the instrument in the temperature range between 470 and 820 °C was determined with the standards CsCl, K_2CrO_4 and $BaCO_3$.[18,19] The temperature dependence of the calibration coefficient, shown in Figure 1, is described by Eq. 5.

$$K(T) = -0.51 + 0.0037\,T \qquad (5)$$

T: temperature (°C)

The phase composition of the samples was determined by X-ray powder diffraction (Cu Kα radiation, Philips PW 1710).

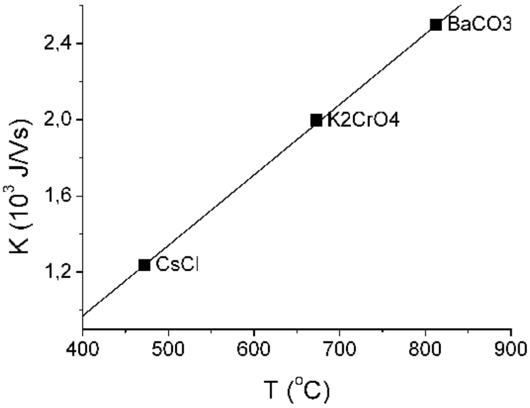

Figure 1. Temperature dependence of the calibration coefficient K.

Results and discussion

The thermoanalysis TG/EGA/DTA curves of the as-dried PZT precursor are shown in Figure 2. The sample loses 22% mass upon heating to 575 °C. The thermal decomposition occurs stepwise: the mass loss from room temperature to 170 °C is 6.4%, from 170 to 331 °C 11.4%, from 331 to 440 °C 2.3% and upon further heating to 575 °C 2.0%. The thermal effects recorded by DTA include a broad weak endothermic effect at 88 °C, and a succession of exothermic peaks between 180 °C and 600 °C with the strongest peak at 487 °C. We followed the mass peaks of water (m/e^+ 18) and carbon dioxide (m/e^+ 44). Between room temperature and 170 °C, i.e. the first step of mass loss, predominantly water is evolved. In the second two steps of mass loss, between 170 and 440 °C, that correspond to about 60% of the total mass loss, water and carbon dioxide are evolved. Upon further heating to 575 °C only the carbon dioxide peak is detected.

Upon heating to 170 °C evaporation of water and residual solvent occurs as confirmed by a broad endo peak. In further steps of mass loss between 170 and 440 °C the evolution of water and carbon dioxide confirm the oxidation of organic groups in air. The stepwise pathway points to the presence of different or differently bonded organic groups, which, in our case,

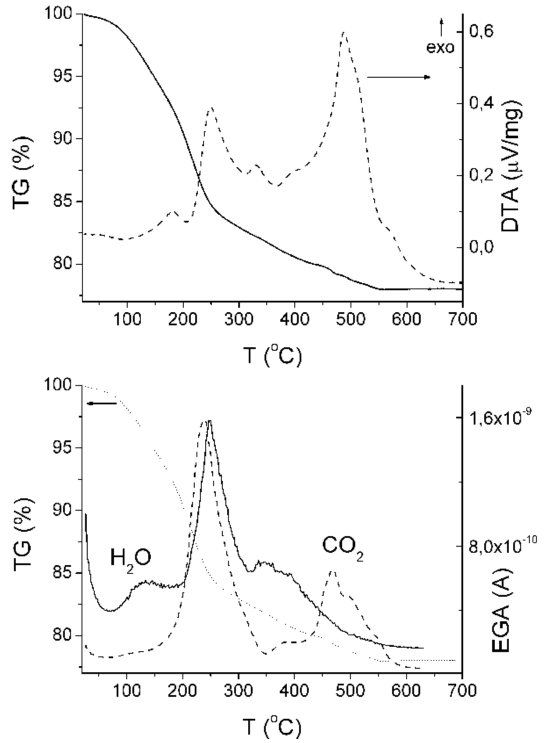

Figure 2. TG/DTA/EGA curves of PZT precursor, dried at 60 °C.

can be either butoxide or methoxyethoxide, as a result of the solvent-exchange (transalcoholysis) reaction.[20] The stepwise decomposition of alkoxide-based precursors is in agreement with literature reports.[9,10,21]

The next step of decomposition, between 440 and 575 °C is mainly a consequence of carbon dioxide evolution as a result of decomposition of carbonaceous species in agreement with the results reported by Coffman et al.[22] Within this temperature range the crystallization of the amorphous sample occurs as confirmed by XRD, namely after heating to 720 °C the sample crystallizes in tetragonal perovskite phase (Figure 3).

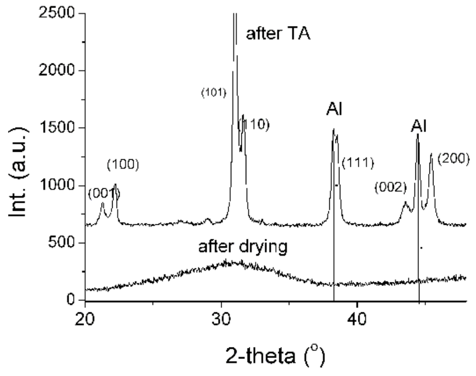

Figure 3. XRD patterns of the PZT precursor after drying at 60 °C and after thermal analysis (TA, heating rate 10 °C/min., final temperature 720 °C). Al: sample holder. The reflections of the perovskite phase are marked.

To further evaluate the crystallization of the PZT precursor we removed the organics by heating the sample at 400 °C.[17] The sample exhibited no further mass loss and it remained amorphous as confirmed by XRD as described later. The DTA curve of the sample heated at 400 °C is shown in Figure 4. We observe a strong exothermic peak between 430 and 520 °C with a maximum at 473 °C and another weak exothermic peak at 551 °C. To explain the presence of two DTA peaks we heated the sample between 400 and 700 °C. Corresponding XRD patterns are shown in Figure 5. Upon heating to 460 °C the sample remains amorphous, while at 480 °C the reflections of the pyrochlore-type phase together with the strongest reflection of the perovskite phase become discernible. After heating to 540 °C the perovskite reflections are more pronounced while the peaks corresponding to the pyrochlore-type phase are diminished. At/above 560 °C only the perovskite phase is identified. In summary, the crystallization of the amorphous PZT precursor occurs via the transitory pyrochlore-type phase, which is stable between 480 in 560 °C. Such crystallization pathway is typical for alkoxide-based PZT precursors.[1,23,24] According to Merkle and Bertagnolli,[24] the two steps of crystallization can not be separated even by changing the heating rates.

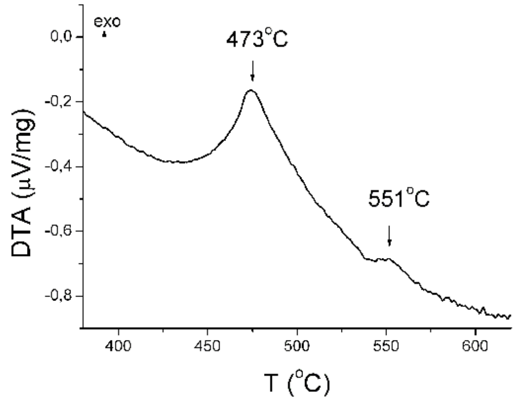

Figure 4. DTA curve of the PZT precursor heated at 400 °C for 5 h. to remove organic residues.

The enthalpy of crystallization of PZT precursor calculated from the DTA peak area (Eq. 4) between 430 and 520 °C is 33 kJ/mol, the relative error of the method is 5–10%.[18]

The enthalpy of crystallization of various alkoxide precursors depends strongly on the synthesis conditions and on composition of the solid solution, that is Zr/Ti ratio. For lead titanate it ranges between 70 and 210 kJ/mol, depending on the lead source.[25] In the case of PZT 30/70, prepared from lead acetate and transition metal propoxides, it equals 12 kJ/mol.[24]

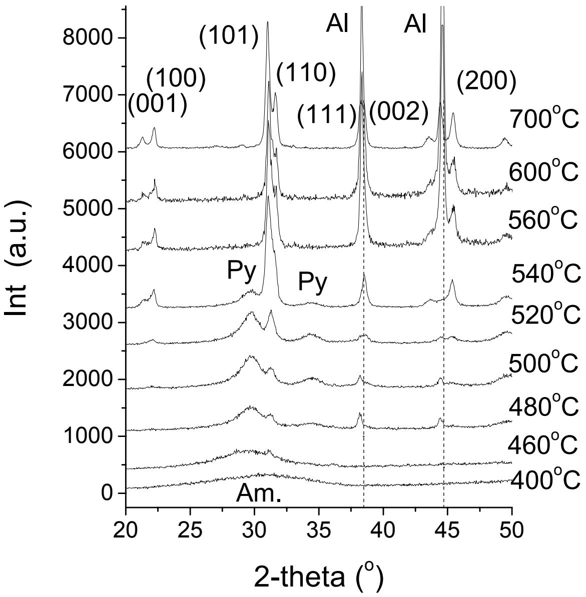

Figure 5. XRD patterns of the PZT precursor heated to the temperatures between 400 °C and 700 °C (heating rate 10 °C/min.). Al: sample holder. Am.: amorphous phase, Py: pyrochlore-type phase. The reflections of the perovskite phase are marked.

The enthalpy calculated from the weak exothermic DTA peak area between 520 °C and 580 °C (Figure 4) is 1.6 kJ/mol. This peak could possibly be due to the growth of the crystals of the perovskite phase. Namely, the perovskite reflections in the samples heated above 540 °C are stronger, i.e. FWHM (full width at half maximum) is decreased, and the splitting due to tetragonal distortion is more pronounced (Figure 5). In the study of the growth of TiO_2 crystals upon anatase–rutile transition Kumar et al.[26] detected two DSC peaks, and they ascribed the stronger peak to the phase transition and the weaker peak equal to 5 kJ/mol to the growth of TiO_2 crystals.

The X-ray patterns (Figure 5) reveal a weak (101) reflection of the perovskite phase after heating to 460 °C. In bulk powder the crystallization from the amorphous phase occurs by homogeneous nucleation. However in the case of thin films the heterogeneous nucleation on the substrate is expected.[27] We therefore followed the phase composition of the PZT film deposited on $Pt(111)/TiO_2/SiO_2/Si$ substrate upon heating (Figure 6). At 350 °C the film is amorphous, at 375 °C the amorphous and the perovskite phase with (111) preferred orientation coexist. After heating at 400 °C the thin film is completely perovskite. In the thin film the perovskite phase crystallizes directly from the amorphous phase, in contrast to what we observed in bulk, where the transitory pyrochlore-type phase appeared between 480 and 560 °C (refer to Figure 5). Generally, the crystallization of the amorphous PZT precursors both in bulk and thin film form occurs via the pyrochlore–type phase, however, the range of its stability has been reported to be above 450/500 °C.[1,23,24] The direct transition of the amorphous to perovskite phase has been reported for lead titanate thin films on Pt/Si substrates,[28] but in the case of PZT 53/47 thin films only when deposited on $SrTiO_3$ (100) substrate which exhibits a perfect agreement of lattice parameters.[14] We propose that in the case of the PZT thin film heated at as low as 375 °C the pyrochlore-type phase is not a stable phase; this could explain the rarely encountered coexistence of amorphous and perovskite phases.

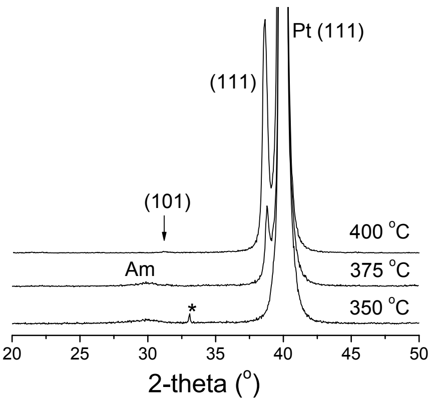

Figure 6. XRD patterns of the PZT film deposited on platinized silicon substrate and thermally treated at selected temperatures for 30 minutes. Am.: amorphous phase. The reflections of the perovskite phase are marked. *: substrate

Conclusions

The as-dried $Pb(Zr_{0.30}Ti_{0.70})O_3$ (PZT) precursor, prepared from lead oxide and transition metal butoxides in 2-methoxyethanol, decomposes upon heating from room temperature to about 600 °C in air by the following steps: evaporation of residual solvents, decomposition of organic groups and of carbonaceous species. The crystallization of the perovskite phase which coincides with the final mass loss occurs through the transitory pyrochlore-type phase, according to DTA the onset of crystallization is at 430 °C. The enthalpy of crystallization is 33 kJ/mol. In the case of the PZT thin film deposited on Pt(111)/Si substrate the crystallization temperature of the perovskite phase is further decreased as a consequence of the heterogeneous nucleation on the platinum surface: the reflections of the perovskite phase coincide with a broad peak of the amorphous phase at as low as 375 °C.

Acknowledgements

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Povzetek

Študirali smo termični razpad in kristalizacijo alkoksidnega prekurzorja $Pb(Zr_{0.30}Ti_{0.70})O_3$ za pripravo tankih plasti iz raztopin. Prekurzor smo pripravili iz svinčevega oksida ter cirkonijevega in titanovega n-butoksida v 2-metoksietanolu. S simultano termično analizo in rentgensko praškovno analizo smo spremljali razpad amorfnega prekurzorja, sušenega pri 60 °C. Le-ta poteče v zraku v večih stopnjah: izhajanju fizikalno vezanih topil sledi razpad organskih skupin med 200 in 440 °C, razpad karbonatnih skupin in kristalizacija perovskitne faze med 440 in 600 ºC. Za študij kristalizacije z diferenčno termično analizo smo prekurzorju predhodno odstranili organske skupine s segrevanjem pri 400 °C, vzorec ostane pri tem rentgensko amorfen. Entalpija kristalizacije perovskitne faze, ki poteče preko prehodne faze piroklornega tipa, je 33 kJ/mol.

Tanke plasti $Pb(Zr_{0.30}Ti_{0.70})O_3$ na podlagi Pt(111)/Si kristalizirajo pri nižji temperaturi v primerjavi s samim prekurzorjem, kar je posledica heterogene nukleacije na platinski podlagi. Perovskitna faza z (111) usmerjenostjo kristalizira neposredno iz amorfne faze pri 400 °C.